TEXTBOOKS ON MODERN ANALYTICAL CHEMISTRY

Edited by

CECIL L. WILSON AND RONALD BELCHER

SEMI-MICRO QUANTITATIVE ORGANIC ANALYSIS

RONALD BELCHER

AND

A. L. GODBERT

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Semi-micro quant.

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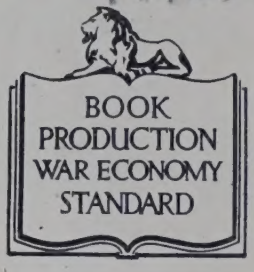

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PREFACE

COMPARED with macro-methods, semi-micro-methods of analysis save time, space and labour. The technique is easier to acquire than that of micro-methods, which is best learnt under the supervision of a skilled micro-analyst. If a chemist has eventually to learn micro-methods, his experience in semi-micro-methods will be a useful stepping-stone.

We felt that there was a need for a textbook containing a complete course in the commoner methods of this type of analysis and have therefore written this book. We have tried out most of the methods described here in competition with other methods having the same purpose, and have also had students try them out to observe how well the methods behaved in the hands of analysts unskilled in them. The methods we chose as the result of these investigations were the simplest of the accurate ones.

We wish to thank Dr. C. L. Wilson for his interest in the book and for suggestions for its improvement. He was good enough, also, to help in the proof reading. For help in the same task our thanks are due also to Dr. H. F. Coward, Acting Director, Safety in Mines Research Board, Dr. J. K. Thompson and Dr. G. H. Wyatt. Finally, we have cause to be grateful to the skill of Mr. C. E. Goodliffe for many of the illustrations and to Messrs. Griffin and Tatlock Ltd. for supplying a number of blocks.

Sheffield,
July 1944.

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SEMI-MICRO QUANTITATIVE ORGANIC ANALYSIS

CHAPTER I

INTRODUCTION

The term *micro* is commonly applied to methods of analysing samples weighing 3 to 5 mg. The term *macro* applies to the analysis of samples of about 500 mg. Semi-micro methods deal with samples of 20 to 50 mg.

In both macro- and micro-methods, the accuracy is usually limited by the efficiency of the methods of analysis, for the samples are weighed to 1 part in 5,000, whereas the methods are unusually exact if they are accurate to 1 part in 1,000. For semi-micro analysis, balances are available in which the same accuracy of weighing may be attained. However, for the analyses described in this book, we have suggested that the analyst should use the ordinary analytical balance for the weighings.

The accuracy of this balance, used, as it often is, as a null-point instrument to weigh to 0·1 mg., would limit the accuracy of the technique of analysis.* To reduce this limitation, the balance should be used to the limit of its sensitivity. Manufacturers are modest about their balances, for which they claim a sensitivity of only 0·1 mg. The sensitivity of a balance in good condition is more than double this and can be fully used by adopting the most efficient method of weighing, the method of swings. The weighing of 20 mg. will attain an accuracy of 1 part in 500 or better, an accuracy about equal to that of the methods of analysis. We assume that the analyst knows little of the method and have described it in some detail. The analyst who is familiar with the method and is confident about the condition of his balance may omit the first part of Chapter II.

After the chapter on the use of the balance, the rest of the book deals with the elementary analysis of organic compounds, the

* Bobranski and Sucharda (1) also adopt the analytical balance in their methods but suggest weighing to only 0·1 mg. Apart from the fact that to weigh to this accuracy represents an inefficient method of using the balance, the weighing introduces from the start too high an error in the analysis; clearly, it may be of the order of 1 part in 200 (using a 20-mg. sample). We may also draw attention to the paper of Niederl *et al* (2) in which the analytical balance is used for micro-analysis. This seems to us to be trying this balance rather high; the balance will have to be in exceptionally good condition to apply it to micro-analysis.

determination of three of their groups, and with certain physico-chemical measurements that may be made on them, particularly to establish their molecular weights. We have thought it worth while, in the following pages, to give a description of these methods of analysis and to indicate where those we have chosen differ, if they do differ, from those customarily described in texts on micro-chemical analysis. This description should serve to give the analyst a general bearing on the methods.

A. DETERMINATION OF ELEMENTS

1. *Determination of moisture, ash and metals.*—The hygroscopic moisture of organic materials is determined by drying the material in a glass tube heated by a metal block, itself heated by a micro bunsen-burner. A stream of inert gas is passed over the material during the drying to prevent oxidation of the sample. The ash of the material is determined by incineration in a hard glass tube over a bunsen-burner. Metals in organic materials are determined as sulphate or oxide by incinerating the material in the same way after moistening it with sulphuric or nitric acid.

2. *Determination of carbon and hydrogen.*—Carbon and hydrogen are determined by Liebig's classical method of burning the material in a combustion tube in a stream of oxygen, collecting the oxidation products (carbon dioxide and water) on weighed absorbents. The various methods published differ chiefly in the means used to ensure that combustion is complete, and to prevent acid products of combustion, such as the oxides of sulphur and nitrogen, from passing to the absorbents. Pregl's filling of the combustion tube for this purpose, a filling often used, is a complex mixture of copper oxide, lead chromate, lead peroxide and silver, packed in the tube itself. We have adopted a simpler filling due to Ingram (3) which can be removed of itself from the tube. It is a mixture of copper oxide, lead chromate and cerium oxide encased in a copper gauze which is inserted in the tube. A boat containing lead peroxide, heated to 180 to 200° C., is used for absorbing the acid products of combustion other than carbon dioxide.

3. *Determination of nitrogen.*—We describe the Kjeldahl and Dumas methods of determining nitrogen in organic materials. The former is to decompose the substance by sulphuric acid, the reaction being catalysed by mercury and selenium. The resulting ammonia is distilled from the solution after making the solution alkaline, collected and determined by titration. The ammonia is collected in boric acid

so that it can be titrated directly. A standard alkali solution is then unnecessary. The Kjeldahl method is not applicable to all organic compounds, but its usefulness may be extended to many compounds which do not respond to the Kjeldahl digestion by reducing them, as suggested by Friedrich (6), with a mixture of hydriodic acid and phosphorus.

In the Dumas method, the substance is burnt, in admixture with copper oxide, in a stream of carbon dioxide. The nitrogen is liberated and its volume is measured after absorption of the carbon dioxide. One difficulty is that some substances leave nitrogenous chars which are difficult to decompose and the results are therefore low. The chars may be burnt in oxygen after the combustion in carbon dioxide is complete. This oxygen may be obtained by heating potassium chlorate previously placed in the tube. We include this useful modification of the method.

4. *Determination of sulphur.*—Three methods for determining sulphur are usually described in text-books on organic analysis. They are (1) combustion in a tube and absorption of the sulphur oxides in hydrogen peroxide; (2) oxidation by nitric acid in a sealed pressure tube; (3) fusion with a mixture of potassium nitrate, sodium peroxide and sugar in a metal bomb. The sulphate in the products is usually determined gravimetrically as barium sulphate.

Of these methods we describe only the first. The estimation of the sulphate gravimetrically is tedious and we have substituted for it a titrimetric method; the solution of sulphate obtained from the combustion is precipitated by an excess of barium chloride solution of known strength, the excess barium is precipitated by potassium dichromate and the barium chromate is estimated by standard ferrous ammonium sulphate. To this method we add the rapid Schöberl method (10), in which the material is burnt in a rapid stream of air, its oxidation being completed upon a sintered silica disc. The sulphur oxides are collected in hydrogen peroxide in which the sulphate is determined as above.

5. *Determination of halogens.*—Similar methods to the three mentioned for the determination of sulphur are usually described for the estimation of halogens. To these may be added for chlorine and bromine, the Zacherl-Krainick method (11) of decomposing the material with concentrated sulphuric acid in presence of potassium and silver dichromates in a stream of oxygen, collecting the halogen evolved in a standard solution of caustic soda containing hydrogen peroxide, and titrating the excess of caustic soda.

The halogen is customarily determined in the products, from combustion or decomposition, as the silver halide.

Of the foregoing methods, we describe only that of combustion in

a tube, for this method best lends itself to the titrimetric estimation of the halide in the products. We adopt the Bobranski-Sucharda (1) method for the determination of chlorine and bromine. The products of combustion are passed over a hot platinum contact to complete their oxidation and the halogens in them are absorbed in hot barium carbonate. The barium halide in the carbonate is dissolved out and determined by titration with a standard solution of silver nitrate, using an adsorption indicator for recognising the end-point.

For estimating iodine, we adopt the method of burning the material in a combustion tube in a stream of oxygen, completing the combustion by passing the gases over platinum contacts, and absorbing the iodine-laden gases in a solution of caustic soda. The iodide in solution is oxidised to iodate and estimated by liberating the iodine in the iodate by interaction with an acidified solution of potassium iodide. The iodine so liberated is determined by titration with a standard solution of sodium thiosulphate.

6. *Determination of phosphorus.*—Phosphorus may be determined by fusion with suitable oxidising mixtures in a combustion tube or bomb, or by digestion with a mixture of sulphuric and nitric acids. We describe only the second of these methods.

After conversion of the phosphorus to phosphoric acid, it is most commonly determined by precipitation as ammonium phospho-molybdate, which is estimated either gravimetrically or by a titrimetric method which consists of dissolving the precipitate in excess of standard alkali and then titrating back with standard acid. Both procedures are slow, for the precipitate has to be allowed to stand at least six hours before estimation by either method. Moreover, the precipitation is subject to interference by, for example, occlusion, so that for accuracy it is necessary to work under strictly defined conditions and to apply an empirical conversion factor for calculating the weight of phosphorus.

In place of this precipitation we describe the precipitation of the phosphorus by means of a complex cobaltammine. In this precipitation the process is completed immediately, and the precipitate may be filtered and weighed soon afterwards. This method saves time. Moreover, the factor for converting the weight of precipitate to the weight of phosphorus is low, so that the estimation is for that reason very accurate.

7. *Determination of arsenic.*—Arsenic in organic compounds may be determined by methods similar to those used for phosphorus. We describe the method of decomposing the material in a small amount of nitric and sulphuric acids. The resulting arsenic acid is reduced by potassium iodide and the iodine liberated is titrated with thiosulphate solution.

B. GROUP ESTIMATIONS

Estimations of the carboxyl, acetyl and methoxyl groups are described.

1. *Carboxyl group.*—The carboxyl is determined by titration with standard alkali.

2. *Methoxyl group.*—The methoxyl group is determined by boiling with hydriodic acid : the resulting methyl iodide is distilled into a solution of bromine to convert it to iodic acid, the excess bromine is removed, potassium iodide added and the liberated iodine titrated with standard thiosulphate.

3. *Acetyl group.*—The acetyl group is determined by hydrolysing with ethanolic or butanolic caustic potash, distilling the resulting acetic acid and titrating the distillate with standard caustic potash using phenol red as indicator. For this determination we use the simple apparatus due to Clark (12).

C. PHYSICO-CHEMICAL DETERMINATIONS

The following semi-micro physical determinations are described :

1. *Determination of the density of liquids.*—The density of a liquid is determined by weighing a known volume of it, about 0·01 ml., in a graduated capillary pipette.

2. *Determination of melting-points.*—We have thought it worth while to describe in some detail the conventional method of determining the melting-points of solids, because of its use in the cryoscopic method of determining molecular weights of material.

3. *Determination of boiling-points.*—We describe two methods of determining boiling-points. In the method of Emich (14) a drop of the liquid is confined in a capillary tube so as to imprison a bubble of air. On heating the capillary in a bath of a suitable liquid, the gas bubble forces the drop up the capillary. The boiling-point is reached when the drop of liquid reaches the surface of the liquid in the bath. In the Siwoloboff method (15) the liquid is also confined in a capillary; inserted in the liquid is another capillary at the bottom of which is a chamber of air. On heating, the air in this chamber expands, and bubbles from it periodically rise through the liquid. At the boiling-point, this air releases the vapour of the liquid so that the slow bubbling becomes a thread of rapid bubbles.

4. *Determinations of molecular weight.*—Three methods for determining molecular weights are described.

a. The ebullioscopic method.—In this the rise in boiling-point of a solvent due to a known concentration of the test material

dissolved in it is determined. The efficient apparatus of Bobranski and Sucharda (1) is described for the purpose.

b. The cryoscopic method.—In this the lowering of the melting-point of a solvent due to a known concentration of the test material dissolved in it is determined. The Rast method, which uses camphor as solvent is most suitable for the purpose and is described. The advantage of the method lies in the high molal freezing-point, lowering constant of the camphor. This is so high that a thermometer which can be read to 0·2° and an ordinary melting-point apparatus can be used for the purpose.

c. Vaporimetric method for liquids.—The method described is essentially the Victor Meyer method, in which a known weight of liquid is vaporised and the volume of vapour measured. A simple apparatus due to Bratton and Lochte (16) is described.

ACCURACY

The accuracy attainable in the various determinations may be indicated. The following absolute accuracies should be readily attainable by a practised analyst.

Elements.

Carbon and Hydrogen:	± 0·2 per cent.
Nitrogen: Kjeldahl:	± 0·2 ,, ,,
Nitrogen: Dumas:	± 0·2 ,, ,,
Sulphur:	± 0·2 ,, ,,
Halogens:	± 0·2 ,, ,,
Phosphorus:	± 0·1 ,, ,,
Arsenic:	± 0·1 ,, ,,

Groups.

Carboxyl:	± 0·5 ,, ,,
Methoxyl:	± 0·3 ,, ,,
Acetyl:	± 0·5 ,, ,,

Molecular Weights.

Ebullioscopic:	± 5 ,, ,,
Cryoscopic:	± 5 ,, ,,
Vaporimetric:	± 5 ,, ,,

The purpose of an elementary analysis of an organic compound is, as a rule, to enable its empirical formula to be deduced. For this purpose the above values of the accuracies may be taken as those necessary when the elements are present in average proportions. If the proportions are low, a higher accuracy should be aimed at. For

example, if less than 3 per cent. of hydrogen is present, an attempt to determine it to within 0·1 per cent. should be made.

Descriptions of the methods and apparatus.—The writer describing a method of analysis is always in a dilemma as to the detail which his description should contain. We believe we have given sufficient detail to enable the analyst soon to master the method.

Our descriptions of the necessary apparatus are usually only general, for most of it can be bought. Any apparatus not, so far as we know, marketed we have described in some detail to enable it to be made.

CHAPTER 2

THE BALANCE AND METHODS OF WEIGHING

BALANCES specially adapted for semi-micro analysis are on the market, but the ordinary analytical balance may be used if it is in good condition and its sensitivity has been adjusted to a suitable value. We shall assume, in what follows, that the analyst is familiar with the principles and general anatomy of the balance.

Observance of the familiar rules for the setting up of the balance and its general use is especially necessary for work on the small scale. We may remind the analyst that the balance, which may be situated in the room in which the analysis is done, should stand on a bench reasonably free from vibrations. The best support is a stone slab supported by stout angle-brackets cemented into the wall. A rubber support between the angle-brackets and the feet of the balance will mitigate external vibrations. The balance should be in such a position that it is not likely to undergo much change of temperature. It should be remote from radiators and windows, it should not be exposed either to direct sunlight or to draughts and should not receive radiations from combustion furnaces and other sources of heat.

The door of the balance case should normally be kept closed and it is advisable for the analyst to keep away from the balance when he is not using it.

Scrupulous cleanliness is essential. The balance and the floor of the balance case should be kept clean. Before any weighing is made, the pans should be brushed lightly with a marten-hair or camel-hair brush. Samples spilt upon the floor of the balance should not be allowed to remain there. Weights should be handled with bone-tipped forceps, and the rider should be kept flat and in good shape.

DISMANTLING AND CLEANING OF THE BALANCE

Before being used for semi-micro analysis, the balance should be cleaned and its accuracy determined. The cleaning of the balance, though simple, is an important part of the analyst's technique, since, for this type of analysis, it should be kept in condition by cleaning it about fortnightly or when it shows signs of becoming less sensitive or of sticking.

When cleaning the balance and its parts, chamois leather gloves or finger tips should be worn. A few pieces of chamois leather, some pointed match-sticks, ivory-tipped forceps and large camel-hair and small marten-hair brushes are required.

The balance is first dismantled as follows. The sliding front is raised away from the case and laid flat on top of it. The glass surface is wiped with a dry lintless cloth to give a clean surface for receiving the parts of the balance. The pans are taken from their stirrups and placed on this surface, the right pan to the right, the left pan to the left. The end knife-edges to which the stirrups are attached are next removed and placed beside their pans. Finally, the beam and pointer are removed by taking hold of the pointer between the thumb and first two fingers near its upper end and lifting the beam from its seating on the central agate plane. Care should be taken not to bend or knock the pointer in so doing. The beam and pointer are likewise placed on the sliding door resting on top of the balance so that the beam lies on the surface and the pointer projects into the air.

The central column of the balance and the frame are first brushed with a small marten-hair brush and then the inside and bottom of the balance case brushed with a large camel-hair brush and chamois leather. The cams under the base which operate the release mechanism are oiled with a drop of light oil applied from a thin glass rod. The balance is then levelled by turning the adjustment screws beneath the case until the bob behind the central column of the balance is vertically above its fixed pointer. The central agate plate of the fulcrum is then wiped with a small piece of chamois leather wrapped round a match-stick and lightly brushed with a marten-hair brush.

To clean the beam, it is held near the top of the pointer and the whole of the surfaces brushed with a small brush. Then the two knife-edges are wiped with a chamois wrapped round a match-stick or over forceps. The beam is inspected for dust and fibres and replaced in its seating, taking care that the pointer is not knocked. During the replacement of the beam, the balance should, of course, be arrested.

The agate plates of the stirrups are wiped with chamois, as described above, and brushed lightly. After inspecting them for dust, they are replaced in their seatings above the knife-edges of the beam. Finally, the pans and their wire supports are wiped with chamois, brushed and hooked into the stirrups. Care should be taken that the stirrups and pans go to their proper sides of the balance. The rider is now carefully brushed. It is then flattened so that its legs are in one plane by pressing it between the folds of fairly stout paper. Finally, it is carefully placed in the rider carrier without distorting it.

The analyst may now proceed to make the tests of the accuracy of the balance to ascertain whether it is suitable for this method of analysis. As these tests depend on a knowledge of the characteristics of the balance, we shall describe these characteristics and their determination first.

DETERMINATION AND ADJUSTMENT OF THE EQUILIBRIUM AND SENSITIVITY OF THE BALANCE

The analytical balance is commonly used as a null-point instrument to weigh 0·1 mg. Standard masses are placed on the right pan to balance the body to be weighed, the test mass, to the nearest 10 mg. The residual mass in units and tenths of a mg. is obtained by means of the rider. For this purpose, the beam of the balance is divided into 50 or 100 parts over that length of it which corresponds to exactly 10 mg. This length of beam may be either half the total length of the beam from the centre to the extreme end or the whole length of beam from the extreme left end to the extreme right end. If half the beam corresponds to 10 mg., a 10 mg. rider is used ; if the whole beam corresponds to 10 mg., a 5 mg. rider is used. If this length is divided into 100 parts, the nearest hundredth part of 10 mg., that is to say, the nearest 0·1 mg., can be obtained directly, if into 50 parts, the nearest 0·2 mg. can be obtained directly and the nearest 0·1 mg. by estimation. To obtain, then, the units and tenths of a mg. of the residual mass, when the weight to the nearest 10 mg. has been obtained by standard masses on the pan, the rider is moved to different points along the beam until that point is found at which the balance is most nearly in equilibrium as shown by the movement of the pointer over its scale.

In general, this null-point method is a rather inefficient way of using the balance, for though it gives the weight to 0·1 mg. and though a sensitivity of only 0·1 mg. is claimed for this type of balance, the sensitivity is always greater, if the balance is in good condition, and should be about 0·01 mg. In order to use the balance efficiently and to estimate, as is desirable for semi-micro analysis, the weight of a test mass to the nearest 0·01 to 0·02 mg., the method of swings must be used. The method, briefly, is as follows. By experiment, the equivalence of the swings in mg. of the pointer across its scale—the sensitivity of the balance—is obtained. The test mass is balanced to the nearest 10 mg. by standard masses on the pans. Then the test mass is further balanced to the nearest 1 mg. (and not to the nearest 0·1 mg. as in the null-point method) by means of the rider by moving it between the different gross tenths-divisions of the graduations on the beam, the one hundredths-divisions being ignored. When the nearest 1 mg. division has so been found, the weight to the fraction of a milligramme is estimated by allowing the balance to swing freely and determining the excess of swing to one or the other side. The equivalence of this swing in milligrammes is then calculated from the known sensitivity of the balance and added to or subtracted from the weight as given by the standard masses on the pan and the position of the rider on the beam.

Before describing in detail the method of weighing by swings, it is

necessary to make some remarks on the method which we recommend for reading the swings the pointer makes over its scale. The convention follows the custom of the micro-chemist. The central division on the pointer scale, where the pointer stops when the balance is at rest, is taken as zero. The scale is divided into 5 or 10 equal divisions on each side of this zero graduation. Instead of reading in terms of the marked divisions as units, each marked division is taken as equivalent to a reading of 10 units and the units of the swing are estimated by mentally dividing it into 10 parts. The suggested convention, therefore, gives a scale reading ten times the nominal reading obtained by taking the marked division as units. A swing that extends just to the fifth marked division will be reckoned as 50 ; one extending 0·7 of a marked division beyond the second mark (a nominal reading of 2·7) will be reckoned as 27.

The rest point of the balance is the excess of swing of the pointer to one or other side of the central mark of the pointer scale when the balance is unloaded. It is determined by the following way.

As in all weighings, the analyst should sit directly in front of the balance. If the balance has a 5 mg. rider, the rider is placed on the zero mark of the beam at its extreme left end. Care should be taken that the rider is seated vertically on the beam so that, looking at it in front of one's eyes, it appears as a straight line, which, being vertical, covers the graduation on the beam. Care is needed in this operation. Time is well spent in getting the rider into good shape for sitting evenly on the beam; a badly-shaped rider may be a source of considerable annoyance. If a 10 mg. rider is used it is naturally removed from the beam during the determination of the rest point.

The door of the balance is closed and the balance beam set swinging by turning the handle or knob on the balance for that purpose. The handle release is usually placed on the left of the case. If so, when turning it with the left hand, the right hand should be placed on the other side of the balance case, so that the two hands are more or less symmetrically disposed with respect to the balance. This reduces any asymmetry of the temperature distribution within the balance case due to the heat of one hand. It should be taken as a general rule, during a weighing, that if the manipulation requires that one hand should approach the balance case, for example, when using the rider carrier, at one side, the other hand should be placed during this time at the other side to offset the effect of the first hand on the balance. If the release knob is at the front, this precaution is, of course, unnecessary.

The beam should be released very gently and slowly. If the pans swing out from the vertical through their suspensions, the beam should be arrested so that the pans are caught near their centre by the pan stops and again slowly released. This process is repeated until the pans have no appreciable swing. When properly released, the amplitude

through which the pointer moves should be small and the movement of the pointer a smooth one. If the swing exceeds five marked divisions of the pointer scale (a scale reading of 50) from the zero mark, the balance should be allowed to swing until the amplitude is below this value.

Even if the swings are small from the start, the first two or three should be ignored and then the scale readings of the limits of the next three swings taken, two to the left and one to the right. Swings to the left of the zero mark on the scale are taken as negative and swings to the right as positive. The average of the two swings to the left is added algebraically to the swing to the right. This sum, for our purpose, is the rest point.*

Though it is to a certain extent immaterial what the rest point happens to be, it is convenient that it should approximate to zero and not exceed a scale reading (positive or negative) of 10. If the determined rest point is greater than this, it is advisable to reduce it by moving the nuts on the adjustment screws provided on the balance for changing the masses of the two sides of the balance. By trial, determining the rest point after each adjustment of the nuts, positions may be found at which the rest point is reasonably small. The frequent placing of the hand within the balance case will set convections current circulating within it. After the adjustment has been made, it is therefore advisable to leave the balance-case open for about 10 minutes in order that the temperature should come to equilibrium, and then to verify the rest point.

The sensitivity of the balance.—In practice, the sensitivity of the balance is defined as the change in the pointer reading caused by an excess of 1 mg. on one side of the balance beam. The sensitivity depends on the weight on the pans, and must, therefore, be determined for different loads. The determination is made in the following way.

When the rest point has been finally adjusted and determined, the balance-beam is arrested and the rider moved from the zero division on the beam to the 1 mg. division, that is to say, to the first *major* division. Care should again be taken to see that the rider is vertical on the beam. The balance is set swinging and the rest point redetermined by allowing the beam to swing several times and calculating it as above from the readings of two swings to the left and the reading of one to the right. This new rest point will be farther to the left on the pointer scale than it was with the rider on the zero mark of the beam. The sensitivity of the balance (in this instance with zero load on the balance) is the difference between the two rest points. Thus, if the rest point with the rider at the zero mark has a scale reading of

* Though not, in a strict sense, the rest point, this definition conforms with the determination, given below, of the sensitivity of the balance and any fault in it is unimportant.

−5 and the rest point with the rider at the 1 mg. mark on the beam has a scale reading of −52, the sensitivity is −52 − (−5) = −47 units of scale reading per mg.

A suitable value of the sensitivity is a scale reading of about 50 per mg. If the sensitivity of the balance is unduly low, it may be adjusted by moving the "gravity" bob found on some balances on the pointer, or the "gravity" nut found on other balances on a vertical arm on the upper framework of the beam. The sensitivity of the balance is increased by raising the gravity bob or nut since this raises the centre of gravity of the beam. The correct position of the nut is found by trial; the sensitivity of the balance is determined after each trial movement of the nut until a satisfactory value is obtained. In these determinations the rest point with the rider on the zero mark of the beam is determined, as well as the rest point with the rider on the 1 mg. mark, since the first rest point may change when the position of the gravity bob is moved.

After adjusting the sensitivity and finally determining it with the balance unloaded, it is also determined, without making any further changes in the balance, with the 1 g. weight on both pans, and then in succession 2 g., 5 g., 10 g., 20 g. and 50 g. weights on both pans. The weights should be put on the two pans as close to the centre as possible so that they will exert no force on them tending to make the pans swing outwards. The beam should be released gently, as described above, so that the pans move only slowly and vertically and with the pointer making only a small amplitude over its scale. The two weights of the same nominal mass will probably not exactly balance one another and will need to be balanced to the nearest milligramme by moving the rider to the various milligramme marks on the beam, testing the balance at each move, until the position giving the closest approach to equilibrium is found. The rest point is then determined. The rider is moved to the next milligramme mark on the beam and the new rest point of the balance determined. The difference between the two rest points is the sensitivity of the balance at the load on each pan. The values of the sensitivity in scale divisions per mg. for the weights listed above should be graphed against the load. From this curve, the sensitivity at any known load can be at once obtained.

TESTING THE CONDITION OF THE BALANCE

Kreider (17) gives the following tests for assessing the condition of a balance. They cover the above determinations, with others which it is desirable to make.

1. The rest point should be constant for a given load on the pans when the masses on the pans are equal and the balance must be of the

proper degree of sensitivity. To test these points Kreider uses the Gauss method of double weighing, which is more efficient than the above method. Two sets of weights are required, though with some inconvenience one set only may be used, making up a given weight from the other weights in the box, for example, the 10 g. weight being balanced by the 5, 2 and three 1 g. weights from the box. Let the two sets of weights be W_1 and W_2. The weights used are 0, 10, 20, 50 and 100 g. The specified weight from set W_1 is put on the left pan and the weight of the same nominal mass from set W_2 on the right pan. The rest point of the balance with the rider on the most favourable milligramme mark of the beam is determined. Let this rest point be A. The weights are interchanged, weight W_1 being put on the right pan and W_2 on the left. The rest point is again determined. Let this be rest point B. To determine the sensitivity with the weights still in the same position the rider is now moved to increase the weight of the right side of the balance by 1 mg.: it is shifted 1 mg. to the right along the beam. The rest point, which is now C, is again taken. The average rest point with the weights interchanged, that is, $\frac{1}{2}(A + B)$, is calculated and the sensitivity $S = B - C$, also, for various loads on the pans.

In a perfect balance, which none is, the values of the average rest point will be constant. In practice, it will vary, but should not vary between loads of 0 and 50 gm. by more than 5 on our conventional method of reading the pointer scale, that is, by no more than half a division on the pointer scale. With a sensitivity of, say, 30 at a 50 gm. load and a shift of 5 in the average rest point, the error in determining a 50 gm. load will be $5/30 = 0{\cdot}17$ mg.

The effect of changing the position of the masses from the centres of the pans to the edges on the rest point should also be determined. If there is any appreciable change when the weights are so shifted on the pans it suggests defects in the terminal knife-edges. The condition of the knife-edges may also be checked by using swings of both small amplitude and of large amplitude in determining the rest point. Any difference resulting in the average rest point from change in the amplitude of the swing again suggests faults in the knife-edges.

As regards sensitivity, we have already seen that for semi-micro analytical work, the sensitivity should be about 50 at zero load. If the balance is in good condition, the sensitivity should decrease only slowly and regularly with increase in the load. In general the balance should not be used for loads greater than that at which the sensitivity is only 50 per cent. of that at zero load; with a sensitivity of 50 at zero load, no loads at which the sensitivity is lower than 25 should be put on the pans. In most semi-micro analytical work, this condition is easily fulfilled.

2. The balance should give weighings that are closely reproducible. For testing the balance in this respect, its precision is determined by

weighing a suitable object ten times. Each of the weighings should be a virtually complete one. It is not sufficient, after making one weighing, to arrest the balance and then, for the next weighing, simply to release it. Between weighings the positions of the weights on the balance should be moved and the rider should be taken from the beam and replaced as carefully as possible, so that it is upright on the beam of the balance. For some weighings, the weights should be grouped, as they normally should be grouped in weighing, near the centre of the pan, the largest weight being in the middle. This minimises the undesirable oscillations which are likely to occur when the weights are distributed haphazardly over the pan. For others of the replicate weighings, however, the weights should be distributed toward the edge of the pan. Each weighing is done by the method of swings. The average of the weighings is calculated, the difference between each of the weighings found and the average of these differences (all taken as positive) is the precision of the balance. It is worth while determining the precision with different loads on the pans. The precision of the balance should not be worse than 0·04 mg., that is to say, the values should always check within 0·2 of a division on the pointer scale if the sensitivity the balance is approximately 50.

3. The balance should have arms of equal length. The precision of an analytical balance chiefly depends on the fact that the arms are of equal length. How far the balance-arms satisfy this condition depends on the excellence of the workmanship that went into the manufacture of the balance. The degree of equality of the balance-arms may be tested as follows. A weight, say, 20 gm., is put on the left pan and balanced by other weights from the same set on the right pan. Let the weights used for the balancing be W. The 20 gm. weight is now put on the right pan and again balanced with weights from the same set. Let the sum of the weights used for this second balancing be W′. Their difference is d, say ($d = \mathrm{W}' - \mathrm{W}$), d being small. Then it can be shown that the ratio of the lengths r and l of the right and left arms of the balance is approximately given by $r : l = 1 + d/2\mathrm{W}$ (paying due regard to the sign of d). In a good balance, $d/2\mathrm{W}$ should not exceed 0·00002, a difference which will have negligible effect on analytical results.

WEIGHING

Before beginning a series of weighings, the balance is allowed to remain open for 10 minutes so that it may come to temperature equilibrium. Before weighing an object, the rest point of the unloaded balance is usually determined. This rest point should be determined if, between successive weighing of the object, more than about 10 minutes will elapse. It is unnecessary if weighings are done more

rapidly, as when weighing out material for analysis in a platinum boat, in which case the whole of the necessary weighings can be done in about 5 minutes.

If the rest point has to be determined, it is determined in the way described earlier, with the balance unloaded and the rider on its zero mark, just before the weighing proper is made.

The object to be weighed is usually put on the left pan of the balance and the weights on the right. All containers in semi-micro analysis—platinum or porcelain boats, glass scoops, tubes for absorbing and weighing products of combustion, such as carbon dixoide and water—are first counterpoised by suitable tares to within a few milligrammes of the true weight. Substantially, only the weight of material added to the container is, therefore, estimated by means of weights proper and the rider. (Suitable counterpoises for the various weighing vessels used in the analysis are listed and described in the section, *Counterpoises*, p. 20.) The weighing of containers, when partially balanced by counterpoises, should rarely require the use of weights greater than one or two-tenths of a gramme. If a container gradually increases in weight, as an absorption tube for carbon dioxide increases during a series of analyses for carbon contents, the weight of its counterpoise should be adjusted fairly often. During a run of carbon analyses, for example, the weight of the counterpoise of the absorption tube should be adjusted to within a few milligrammes before both the morning and the afternoon work.

In making a weighing, the vessel to be weighed is placed upon the left pan of the balance as symmetrically with respect to the centre of the pan as the eye can judge. The counterpoise is placed at the centre of the right pan. The rider being on the zero mark on the beam, the heaviest weight that is likely to be necessary to balance the vessel is then added to the right pan, being placed close to the counterpoise, and the beam is slightly released. Until the rider is moved to make the final counterbalancing, the beam should not be released more than is necessary to show which side of the balance is the heavier; the pointer should not be allowed to move over more than about two marked divisions of its scale. Weights of appropriate denomination are added to or removed from the pan, according to the direction of the swing of the pointer, until the vessel being weighed is counterbalanced to 10 mg.

The weights should be put on the pan in a systematic order and the smallest number of weights should be used; where there are two weights of the same denomination they should always be used in the same order, and if the weighing demands the use of 20 mg., for example, on the pan, one 20-mg. weight should be used rather than two 10-mg. weights. That the weights should be added always in the same order (and, as a consequence, that the weights should be kept in one order in their box) is necessary to enable the calibration corrections of the

weights to be applied without confusion (see next section). The weights on the pan, when equilibrium has been achieved, are noted and then checked by the vacant spaces in the box. (When the weighing has been completed, a final check may be made when they are removed from the balance-pan and are replaced in the box.)

The final counterbalancing is done by means of the rider, which is moved between the different milligramme divisions of the beam until the best point of balance is obtained. With the rider on the most favourable milligramme mark, the beam is allowed to swing freely and the rest point is determined in the usual way. From this and the sensitivity of the balance at the load on its pans, which must be approximately known, the residual weight equivalent to the swings of the beam is determined. Suppose that the weights on the pan are 0·67 g., that the rider is on the 4 mg. graduation on the beam, and that the excess of swing is 22 to the right. The approximate load on the pans, known from a rough previous weighing is 18 grammes, at which the sensitivity of the balance, from the graph drawn from the results of the sensitivity tests, is 42 per mg. Then the rest point of the balance of 22 is equivalent to $22/42 = 0{\cdot}52$ mg. Hence the weight of the object (excluding the counterpoise) is 0·67 (weights) + 0·004 (rider) + 0·00052 (swings) = 0·67452 gm. The equivalent weight of the swings is added to the rest of the weight, since the swing is to the right and, therefore, positive. If the same swing had been found to the left, its equivalence would have been subtracted from the mass given by the weights on the pan and the rider; the weight would have been 0·67 + 0·004 − 0·00052 = 0·67348.

The analyst will probably find it more convenient to record all weights in terms of milligrammes, and to get into the habit of thinking in terms of milligrammes rather than in terms of grammes. In terms of milligrammes, the rider gives the unit place and the swings the first and second places of decimals. It becomes simple, then, to obtain such a weight as the above by rapid mental calculation as 674·52. This is rather an exceptional weight to be encountered and the analyst will find that his weights will seldom go beyond the tens of mg.

The actual weight of the object should be corrected by the rest point of the balance. But instead of correcting each weight by the rest point determined just before or after it, it is easier to keep the rest point as a separate item and correct any later weighings for any *change* in the rest point. The rest point changes only slowly and, if the balance is favourably situated, only a little over a day.

STANDARDISATION OF THE WEIGHTS

Incorrect weights are probably the chief source of error in weighing. In the analyses described in this book, as in most analytical work, the

important concern is that the relative values of the weights with respect to one another should be accurately known; their absolute values are of no interest. Hence, in correcting the weights, it is only necessary to compare the weights with one of their number which is taken as standard.

The conventional set of weights usually comprises 100 g., 50 g., 20 g., two 10 g., 5 g., 2 g. and three 1 g. weights, and the fractional weights are 0·5 g., 0·2 g., two 0·1 g., 0·05 g., 0·02 g., and two 0·01 g. The semi-micro analyst will find most use for the fractional weights and it is unnecessary to calibrate the weights heavier than 1 g. In the calibration, it is assumed that the rider is correct in its 10 mg. position and the masses of the weights are found in relation to this. The weights are best calibrated by the substitution method. For this purpose it is necessary to have a series of tares, preferably the weights from another box. The method is as follows:

1. The 10 mg. weight of the tare set is put on the left pan and the rider placed to the extreme right end of its beam on the 10 mg. notch. The usual precautions are taken to observe that it is properly seated on or in the 10 mg. mark. Readings of the swings of the balance are taken, discarding the first two complete swings, the excess of swings to one side noted and the corresponding equivalence of this swing in mg. calculated from the sensitivity of the balance at zero load. Let this equivalent weight be d_1.

2. Then the 10 mg. weight of the set to be calibrated is put on the right pan, and the rider put on its zero mark. The swings of the balance are again taken; let the excess deflection be equivalent to d_2 mg.

3. The 10 mg. tare weight on the left pan is replaced by the 20 mg. tare weight, the 10 mg. calibration weight kept on the right pan and the rider moved to the 10 mg. mark on the beam. The difference in mg. of these weights is once more computed from the deflection of the swings of the pointer.

4. The 20 mg. calibration weight is substituted for the 10 mg. calibration weight on the right pan, the rider moved to its zero mark on the balance and the difference in mg. calculated from the deflection.

5. The other 20 mg. weight of the calibration set is tested similarly to the first.

6. For testing the 50 mg. calibration weight, the 50 mg. tare weight is put on the left pan, the two 20 mg. calibration weights on the right pan and the rider on the 10 mg. mark of the beam. The two calibration weights are then replaced by the 50 mg. calibration weight and the rider moved to the zero mark on the beam.

This process is continued with all the weights up to the demonina-

tion of 1 g. The tare weights are kept on the left pan and the calibration weights on the right and the two sets of weights balanced appropriately by moving the rider between its zero and the 10 mg. notch. Continuing the calibration, for example:

7. 100 mg. tare weight on left pan: 50, 20, 20 mg. calibration weights on right pan, rider at 10 mg.
8. 100 mg. tare weight on left pan; 100 mg. calibration weight on right pan, rider at zero mark.
9. 200 mg. tare weight on left pan; 100, 50, 20, 20 mg. calibration weight on right pan, rider at zero mark.
10. 200 mg. tare weight on left pan; first 200 mg. calibration weight on right pan, rider at zero mark.
11. 200 mg. tare weight on left pan; second 200 mg. calibration weight on right pan, rider at zero.

The subsequent procedure is analogous to the procedure for the 50 mg. weight.

We assume that the weight of the rider is correct. Let this be R. Then if T is the weight of the tare, S the weight of the calibration weight, both with respect to the rider, d_1 the difference in mg. with the rider on the 10 mg. mark and d_2 the difference in mg. with the rider on the zero mark, then clearly $T = R + d_1$ and $T = S + d_2$. Whence, $S = R + d_1 - d_2$ (the values of d_1 and d_2 being the algebraic values obtained from the deflections).

The calculations may be conveniently arranged in a table such as the following:

Tare, T, mg.	Rider at 10 mg.			Rider at 0 mg.			
	Calibration weight, S, mg.		Difference, mg., equivalent to deflection.	Calibration weight, mg., nominal value.	Difference, mg., equivalent to deflection.	Corrected weight, mg.	Correction, mg.
	Nominal value.	Corrected value.	d_1		d_2	$S = R + d_1 - d_2$	
10	None	—	−0·03	10	−0·04	10·01	+0·01
20	10	10·01	−0·03	20′	−0·02	19·99	−0·01
20	10	10·01	−0·01	20″	+0·01	20·00	—
50	20′+20″+10	20·00+19·99+10·01=40·00	+0·02	50	+0·02	50·00	—
100	50+20′+20″+10		+0·03	100	−0·03	100·06	+0·06
200	100+50+...+10		+0·01	200′	+0·04	199·97	−0·03
200	100+50+...+10		−0·02	200″	−0·02	200·00	—
500	200′+200″...+10		−0·04	500	−0·03	499·99	−0·01
1000			+0·03	1000	−0·04	1000·07	+0·07

In making the calculations, the corrections of the weights already calibrated are transmitted through the calculations. The 10 mg. calibration weight has a relative mass of 10·01. In using it to balance the 20 mg. calibration weight, this corrected weight of 10·01 mg. is

used in the calculation. The corrected weights of the two 20 mg. weights are 20·00 and 19·99 mg. In using these and the 10 mg. weight to balance the 50 mg. calibration weight, the corrected weights of 20·00, 19·99 and 10·01, or a total of 40·00 mg., are used in calculating the correct weight of the 50 mg. weight.

It will be found convenient to use a table of correction values for the weights, arranged in the manner of the table below. In this table, the differences between the nominal values and the calibration values are used, and for any total sum of weights in the table, the algebraic sum of these differences is computed. In making up any sum of weights for the table, it is assumed that the minimum number of weights is used and that a given weight of a pair of the same nominal value is used first in the balancing. It is for this reason that the weights should always be added to the pan of the balance in the same order.

Mg.	0	10	20	30	40	50	60	70	80	90
0	0	10·01	19·99	30·00	39·99	50·00	60·01	69·99	80·00	89·99
100	100·06	110·07	120·05	130·06	140·05					
200	199·97	209·98								
300	300·03									
400	399·97			etc.						
500										
600										
700										
800										
900										
1000										

Care of the weights.—Weights should be handled only with ivory- or bone-tipped forceps. They should be tested periodically. If subsequent testing shows that their masses have changed substantially, they should be washed with water, followed by alcohol and then polished with a fine cloth. The rider is inclined to change in weight, usually showing an increase. If it does, it should be discarded.

WEIGHING EQUIPMENT

The following equipment is necessary for weighing materials. Other designs of the equipment have been published and may, of course, replace those decribed here ; and the equipment may be supplemented by any tool which the analyst may deem to be desirable.

Counterpoises.—As, in quantitative analysis, we need know only the weight of a sample, the weight of combustion products or the weight of a precipitate, the weighing vessels for these materials are suitably counterpoised and the balance weights used chiefly for estimating the weight of the material. The type of counterpoise that is recommended varies with the type of weighing vessel used. To minimise errors resulting from the buoyancy effect of the air, the counterpoise should

be of material of the same density and be of similar volume to the object—platinum for platinum, glass for glass, and so on. In practice, in semi-micro work, the buoyancy effect causes no appreciable error if the conventional counterpoises are used—aluminium for platinum and glass flasks loaded with lead shot for glass ware.

Suitable counterpoises are the following:

Object to be weighed.	*Counterpoise.*
Platinum boat and similar light objects	Aluminium wire
Porcelain boat	Glass rod or porcelain boat
Glass charging tubes	Glass rod
Absorption tubes	Glass flask with lead or glass shot
Glass weighing pig	Glass flask with lead or glass shot

Aluminium wire of about 1 mm. diameter is used to balance platinum boats. The wire is bent into a spiral shape so as to lie in a small space on the balance-pan, a short end of the wire being left projecting from the spiral to enable the wire to be picked up and manipulated by forceps. The wire is adjusted to the platinum boat by cutting off short lengths of the wire and constantly balancing it against the boat. When the weight of wire is close to that of the boat, the adjustment is completed by carefully filing it until it is about 1 mg. lighter than the boat.

The counterpoise for absorption tubes and charging tubes consists of a small glass flask containing lead or glass shot. These tubes will normally require to be supported on the balance-pan by means of a metal wire or other support. The flask of lead shot is adjusted to balance both the tube and its support. The tube and its support are counterbalanced against the tare flask on the balance by adding shot to or withdrawing them from the flask until the flask and its shot are only 1 mg. or so lighter than the container. In adjusting the tare with shot, it is convenient to have one of the shot on the balance-pan while adding the other pieces of shot to the tare flask. As the counterbalancing becomes more exact, the shot on the pan will have to be replaced by smaller and smaller shot until the best balance is obtained. The shot on the pan is then placed in the flask to complete the counterpoising.

When glass rod is used for counterpoising objects, such as weighing tubes, it is bent into suitable shape so as to be stable when placed on the balance-pan. To make the counterpoise, glass rod (of soft soda glass) of 4 mm. diameter is drawn out at one end in a batswing burner flame until the tail of glass is about 10 cm. long and 1 mm. diameter. The wide end is cut off until the rod is somewhat heavier than the vessel to be counterpoised. Pieces are then cut off the narrow length of rod until the weight is a few milligrammes heavier than the weighing

tube. Final adjustment, so that the rod is about 1 mg. lighter than the object, may be made by filing the narrow end of the rod. The two ends of the rod are smoothed in the bunsen flame and the rod bent into a suitable shape in the flame. For example, its wide end may be softened in the blowpipe flame and flattened by pressing it upon an asbestos board, while the narrow end is melted to a bead, so that the counterpoise finally consists of a narrow cone of glass on a broad base. After bringing the glass to this shape, care should be taken to anneal the glass well in a small luminous bunsen flame.

Forceps: stainless steel forceps, preferably tipped with platinum, are used for handling platinum boats. *Ivory-tipped or bone* forceps are used for handling weights. Chamois-tipped forceps are useful for handling weighing tubes, bottles and glass tares. For tipping metal forceps with chamois leather, the tips of the forceps are heated in the flame of a bunsen-burner, some Faraday cement applied to the tips which should be just so hot that the cement remains molten while a small piece of chamois leather is attached to the inner surface of the tip. The chamois is trimmed when the cement has hardened and the leather is firmly attached to the forceps.

Spatulas. A spatula of the ordinary type and a micro-spatula are required. The micro-spatula is made of stainless steel or nickel silver and has the two ends flattened, the one to a width of about 2 mm. and the other to a width of about 4 mm.

Marten-hair brushes.—Small marten-hair brushes are required for such purposes as removing dust or excess sample from the outside of weighing boats into which the sample has been weighed, and for cleaning the parts of balances.

Camel-hair brushes.—Large camel-hair brushes are required for cleaning the balance-case.

Wire fork.—A wire fork of the kind shown (Fig. 1) is necessary for handling absorption tubes used in the determination of carbon and hydrogen. After cleaning the absorption tubes, they cannot be handled with the bare fingers until they have been weighed. The tubes are placed on the balance-pan, after cleaning, by supporting them in the crotch of the wire frame and transferring them in this position to the balance-pan.

FIG. 1.

Wire rack.—A wire rack of the type shown (Fig. 2A) or one of the common types of penholder in tiers is used for holding glass charging tubes and absorption tubes before they are weighed. For filter-sticks and crucibles a form of rack similar

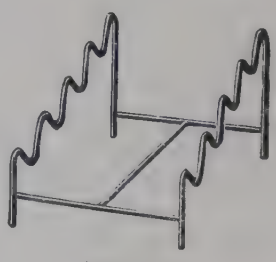

FIG. 2A.

to a test-tube rack is suitable. Such racks are kept near to the balance case on a piece of cardboard.

Wire support for tubes on balance-pan.—The pans of analytical balances are not normally furnished with stirrups for holding absorption and weighing tubes while weighing them. Some form of support is desirable so that these tubes do not roll about the pan. The figure (Fig. 2B) shows a simple support which is suitable for this purpose.

FIG. 2B.

Chamois leather, flannel cloth.—For cleaning glass vessels before weighing them, a few pieces of lintless flannel cloth, moistened with distilled water, and about six pieces of dry chamois leather are necessary. These pieces should measure 10 to 12 cm. square. The chamois leather should be frequently washed by rubbing it beneath the surface of tepid soapy water containing one or two drops of ammonia. It is then washed with distilled water and hung up on a string to dry. When dried, it is rubbed to make it soft again. To protect the flannel and chamois from dust, they are stored in 6-inch Petri dishes. It is absolutely necessary that the chamois leather should be subjected to no other cleaning process than the above.

Chamois leather finger tips or gloves.—For handling glass weighing vessels and for cleaning the balance, the fingers should be encased in either chamois finger tips or gloves. They are cleaned in the way described above.

Cotton wool.—Non-medicated absorbent cotton wool is required for preparing the cotton wads used for cleaning absorption tubes and to form part of their filling.

WEIGHING VESSELS AND PROCEDURES

Sampling materials for analysis.—Micro- and semi-micro analysis are chiefly concerned with the analysis of pure organic materials. Such materials are homogeneous and no difficulties in sampling arise. If the material is heterogeneous, like coal, care has to be taken to obtain a representative sample. If the material is a solution, it should be thoroughly shaken before the sample is taken for analysis. If the material is a solid, sampling is done in the conventional manner, the material being ground to a suitable size, reduced in bulk by quartering and taking opposite quarters of the material spread out on paper, rejecting the other two quarters and grinding further and continuing the quartering until the final sample is obtained. The final sample should be sufficiently fine to pass wholly the 240-mesh (B.S.I.) sieve.

Weighing materials for analysis.—For determining moisture and
contents, carbon and hydrogen contents and sulphur and the halog
by combustion methods, dry solids are weighed in the boat in wh
the analysis is to be made. For determining moisture contents or
weighing hygroscopic solids, the boat which contains the materia
weighed in a weighing pig. For weighing dry solids for estimation
their nitrogen contents by either the Kjeldahl or Dumas methods
for their halogen or sulphur contents by the bomb methods, or
determining the phosphorus or arsenic contents, the solids are weigh
in a charging tube, with or without cap. If the solid is hygrosco
the charging tube has to be provided with a cap. For weighing sol
for determining their nitrogen contents by the Kjeldahl method,
analyst may find it convenient to weigh them on a glass scoop.

The object to be weighed must be at the same temperature as
inside of the balance-case. To attain this equilibrium, it is plac
beside the balance for 5 to 30 minutes before weighing, the ti
required depending on its composition and size. The side doors of
balance should remain open at least 10 minutes before weighing.
currents inside the balance-case, unequal temperatures due to bo
heat of the analyst or adjacent warm objects may cause changes
temperature which must be avoided. As a general rule, it is advisab
to keep away from the balance as much as possible between actu
weighings.

WEIGHING VESSELS

Boats.—Porcelain or, preferably, platinum boats are used f
weighing solids for analysis. The platinum boats are preferable
being more resistant to corrosive reagents, but modern porcelain boa
are almost equally satisfactory. The platinum boats are abo
1·5 cm. long, 5 mm. wide and 4 mm. high. The porcelain boa
available are rather longer but smaller in cross-section: 2 cm. lon
4 mm. wide and 4 mm. high.

After being used in any analysis, the boat is cleaned by boiling
for a few moments in a Pyrex test tube with a 50 per cent. solution
concentrated hydrochloric acid. The boat is removed from the te
tube by means of a platinum wire hook, tilted when out of the ac
to drain off most of the adherent acid, and then held in the outer co
of a non-luminous bunsen flame until it glows bright red. The bo
is then put on the copper block of the micro-desiccator, which is place
near the balance-case.

Weighing in boats.—If the boat is of platinum, it may be weigh
within a minute or so after putting it into the desiccator; if of porc
lain, it is left about 10 minutes in the desiccator to ensure that i
temperature should come to the atmospheric temperature.

In order to weigh it, the boat is transferred through the open door of the case to the left pan of the balance, the counterpoise placed on the right pan with the same forceps, the door of the case closed and the boat weighed by the method of swings. The weight of the boat should be checked twice, removing the rider from the beam and replacing it before re-determining the swing of the pointer. The boat is then removed from the balance-pan and placed on a clean glass plate. About 20 mg. or a suitable amount of the material to be analysed is placed in the boat with a micro-spatula and, if possible, spread over the bottom of the boat. The boat is then picked up with forceps, any material adhering to its outside surfaces brushed off with a small camel-hair brush and again placed on the left pan of the balance. The weight of the boat plus the sample is determined in the same way as the weight of the empty boat. The difference in the two weights gives the weight of the material. The boat containing the sample is then transferred to the micro-desiccator until it is used in the analysis.

If the boat is to be weighed again during the course of the analysis, as, for example, in weighing the residue left in the boat after the combustion of the material, the rest point of the unloaded balance should be determined before weighing the material and also before the boat is re-weighed after the combustion, in order to correct the weight of the residue for any change in this rest point.

If the material in the boat is mixed with a reagent, for example, copper oxide in burning materials difficult to burn, the dried and fine reagent is added to the weighed sample and mixed by means of a short platinum wire. The wire is left in the boat.

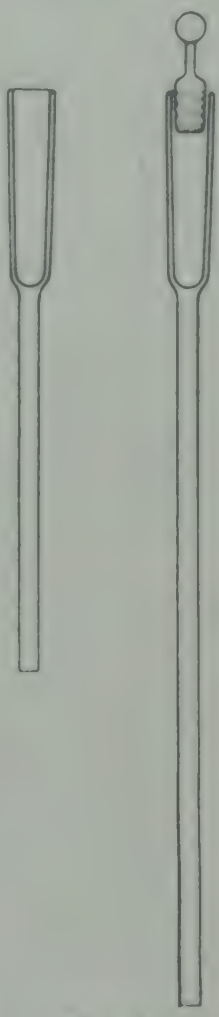

FIG. 3.

Long-stem charging tubes.—A charging tube is used when a solid has to be weighed and then transferred to another vessel such as a Kjeldahl digestion flask. It consists of a soft glass tube of 2 cm. length and 4 mm. internal diameter to which is fused a glass rod about 11 cm. long and 1·5 mm. thick. Two forms of it are illustrated (Fig. 3), one an open tube and the other with the tube closed by a ground-glass cap. The second form is used for weighing hygroscopic materials. Both forms may be bought. The simpler form may be fabricated by softening a piece of soft glass of about 0·8 cm. internal diameter in a batswing flame, blowing the molten tube rather wider by about 2 mm. to reduce the thickness of the walls somewhat and then drawing it out so that the internal diameter is about

4 mm. One end of this prepared tubing is then drawn out in the flame, closed and blown to roundness by allowing the walls to collapse, but without blowing a bulb at this end. A glass rod drawn out in the batswing flame to a diameter of about 1·5 mm. thick and a length of 10 cm. is heated at one end in the fine flame of a blowpipe, while the closed end of the prepared tube is also heated in the flame and the two joined together at the points of heating. The heating is continued until the join is sealed. Finally, the tubular part is cut so that it remains about 2 cm. long.

Weighing in the charging tube.—As the charging tube is of glass, it is more difficult, in general, to obtain agreement in successive weighings of it than with a platinum boat, but the difficulty is only appreciable and the difference in weight only perceptible when weighing on a micro-balance. However, whenever a charging tube has to be weighed, even on the semi-micro scale, it should be left on the balance-pan for five minutes before weighing it.

The charging tube is counterpoised with either glass rod or a small glass flask loaded with lead shot. It is supported on the pan of the balance by means of a notched frame, either of wire or metal sheet (p. 23). When transferring the charging tube to and from the balance, it should be handled by chamois leather, more conveniently by the finger tips covered with chamois tips or best with chamois gloves on the hand. After cleaning the charging tube with a small chamois leather, about 20 mg. of the test material is placed in it with a micro-spatula, the material forced to the bottom of the tube by lightly tapping the end of the tube handle on a clean glass plate and the tube placed on the support on the balance-pan. After allowing the tube to remain on the balance-pan a few minutes, the tube is weighed, using the appropriate glass counterpoise, in the usual way, so that the reading of the weight is completed in not less than 5 minutes. The tube is then removed by means of the wire fork from the balance, grasped with the chamois-covered fingers at its lower end and the contents emptied into the flask or other receptacle which is to hold it. While taking the charging tube from the balance, it is kept in the horizontal position so that none of the material escapes from it while it is being transferred. The flask to which it is to be transferred is also held in a horizontal position while the charging tube is being inserted into its neck and the charging tube so far inserted into the neck that when the tube and flask are brought to the vertical to discharge the contents of the tube, the material finally rests on the bottom of the bulb of the flask and none adheres either to the upper part of the bulb or to the neck of the flask. By carefully tapping the charging tube while it is in the vertical position in the flask, most of the contents can be discharged and few particles will remain in the charging tube.

The flask and charging tube are once more brought to the horizontal position, the tube withdrawn from the flask without touching the sides of the neck of the flask and taken while still in the horizontal position to the balance-pan. It is re-weighed after a few minutes in the usual way to obtain the weight of the sample taken for analysis by the difference in the two weighings of the charging tube.

Glass scoops.—Instead of charging tubes, glass scoops may be used for weighing solid materials to be transferred to reaction vessels after weighing. These scoops are listed by chemical supply houses.

Weighing capillaries.—Weighing capillaries are used for weighing liquids to be analysed. Soft glass tubing of about 1 cm. diameter is softened in the batswing flame, removed from the flame and, with a rotating movement of the two hands, the tubing drawn out to a capillary of 1 to 2 mm. bore. This capillary is cut into lengths of 10 cm. The middle of each capillary is held in the flame of a micro-burner until the walls collapse and form a solid thread, which is drawn out to a diameter of 0·5 mm. and to a length of 3 cm. This thread is further heated in the centre until it separates into two parts, forming two capillaries with handles, the ends of which are fire-polished. At this stage, chemical reagents, such as potassium chlorate for determination of carbon and hydrogen, are introduced into the tube. A crystal of the potassium chlorate is inserted in the open end of the capillary, tapped down to the sealed end and its position fixed there by gentle fusion in the micro-flame. The capillary is then heated in the micro-flame approximately 1·5 cm. from the sealed end and drawn out to a fine capillary of 0·1 mm. bore, thus forming the bulb and delivery stem of the weighing capillary. The fine delivery stem is cut to a length of about 1·5 cm., making sure that the capillary is open. A number of these capillaries should be made at one time and kept in a desiccator over a desiccant.

For volatile liquids, the delivery stem of the capillary is made longer and finer. For viscous liquids or for liquids of high boiling-point a capillary about 10 cm. long is used.

Weighing in capillaries.—To weigh a liquid in a small capillary, after the chemical reagent has been introduced into the capillary and the end of the capillary drawn out and cut off, the capillary is wiped with a piece of chamois leather, put on the metal block of the micro-desiccator and after a minute its weight determined. A small amount of the sample to be analysed is put on a small watch glass, the tube of the capillary gently warmed in a micro-burner flame and the fine end of the delivery stem dipped into the liquid. As the capillary cools the vacuum created in it draws liquid into the capillary. Sufficient of the sample is drawn into it to weigh about 20 mg. If the dimensions of

the capillary are adhered to, the volume of liquid required will fill about half the tube. The liquid thus drawn into the bulb is centrifuged to the bottom of the bulb. The delivery stem of the capillary is then passed through the flame of the micro-burner to evaporate and burn any liquid left on the outside of the tip and to seal the delivery stem. The outside of the capillary is then wiped clean and the capillary re-weighed when cool to obtain the weight of the sample.

An alternative method of filling the capillary is as follows: After weighing it, the open end of the capillary is placed beneath the surface of the small amount of material to be sampled, contained in a small specimen tube or sample bottle. Both are placed in a small filter flask equipped with a rubber stopper through which a tap passes. Suction is applied to the filter flask, which also evacuates the capillary. This only takes a few seconds. The tap to the flask is now slowly opened and the difference in pressure between the outside and inside of the capillary forces the liquid into it.

Weighing pig.—For weighing hygroscopic material before drying it to estimate its moisture content, its container, such as a platinum boat, is placed in a weighing pig and weighed with the pig. For stability, the bottom of the pig at the closed end, the bottom of the feet and the bottom of the rim at the ground joint should be in one plane to provide points at which the pig may rest on a surface. The pig and its contents are counterpoised by means of a flask with lead or glass shot.

CHAPTER III

GENERAL APPARATUS

In addition to the apparatus described in later chapters on the determinations of the elements of organic compounds, such general apparatus as electrically-heated ovens for drying, muffles for incineration, and the common laboratory equipment, such as test-tubes and beakers, ranging from the common sizes to the micro-sizes, will be required and the following apparatus may be specifically mentioned. As most of it is marketed, detailed description is unnecessary.

Desiccators.—The laboratory should be provided with both the conventional sizes of desiccators, ordinary and vacuum, and with one or two micro-desiccators. Pregl's hand desiccator consists of a thick glass container surmounted by a slightly smaller glass top, of similar shape and making a ground-glass connection with it. A thick copper disc is supported by a metal triangle on the rim of the lower container. This copper block serves as an efficient cooling device for such receptacles as platinum boats. No desiccant is used in the desiccator. Niederl describes a similar but smaller desiccator. A round aluminium block, 62 mm. in diameter and 45 mm. high, has a concentric ring, 55 mm. outer diameter, 6 mm. wide and 5 mm. high, cut on its upper surface. A 50-ml. Petri dish of 56 mm. outer diameter and 38 mm. high fits into the outer periphery of this ring and serves as a cover. In its centre the metal block has a conical cavity, 35 mm. wide and 35 mm. deep. This cavity serves as a convenient receptacle for crucibles used for the ignition of precipitates. The rim of this cavity is 5 mm. below the concentric ring and supports a concave copper block of 39 mm. diameter and 12 mm. thick which serves as a support and cooling device.

Burners.—Bunsen-burners of the usual size and of micro-size are required. The micro-burners are on the same principle as the normal type of bunsen-burner. Micro-burners may be made from 1-cm. glass tubing (Pyrex or Jena glass) by drawing it out to a nozzle with a diameter of 1 mm. or less, according to the work for which it is required. Though these glass burners are suitable for some purposes, chief reliance should be put on the metal burners which are available commercially.

For heating the catalyst in combustion tubes in determining the elements, about 16 cm. of the tube, in which the catalyst lies, has to be heated. This is accomplished by means of a long burner. This burner is about 17 cm. long and its flame may be controlled in both

its degree of aeration and in the gas supplied to it, the latter being controlled by a needle valve in the inlet tube. The height of the burner is also adjustable; a lug on the body of the burner makes a sliding fit with the hole in the base of the burner and the body may be fixed at any height by means of a thumb screw after the height of the body has been adjusted.

If the Bobranski-Sucharda automatic regulator for the combustion is used in the determination of carbon and hydrogen, a bunsen-burner of special type fitted with an auxillary pilot jet is necessary for burning off the material.

Heating blocks.—Materials are dried in glass tubes which are heated in " regenerating " blocks. Pregl's heating block is shown in Fig. 4. It consists of two superimposed copper or aluminium blocks, each provided with two semi-circular channels which together form cylindrical canals through the block. One of these channels has a diameter of 13 mm. and serves to hold the central part of the drying tube or filter stick when it is desired to dry precipitates. The second channel has a diameter of 8 mm. and can be used for sublimation tests, etc. The lower block is mounted on a stand approximately 9 cm. high and is heated by a micro-burner integral with the stand. It has a horizontal boring which serves to contain the bulb of a thermometer. The upper block has a heat-insulated handle by which it can be removed from the lower block. Pins projecting from the surfaces of the two blocks and appropriate holes in them to engage with the pins enable the two blocks to be correctly aligned.

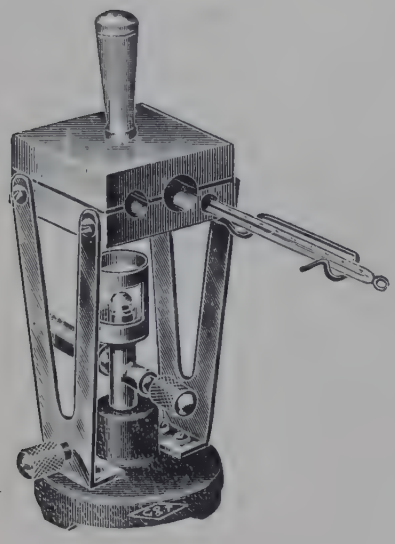

FIG. 4.

Combustion stands.—Combustion stands are required for supporting combustion tubes. The combustion stand is about 30 cm. long and 20 cm. high up to the V-notches at the ends of the stand. The side rails running the length of the stand are U-shaped to receive the wire tunnel of the same length as the long burner which deflects the heat down upon the combustion tube.

Retort stands.—Retort stands are used to support absorption tubes, etc. They are smaller in size than the conventional type and have circular bases. The clamp is attached to the stand by spring jaws. The absorption tubes are supported from metal wires soldered to the clamp.

Centrifuges.—A small hand-operated centrifuge is necessary for centrifuging weighing capillaries. If a small centrifuge cone has to be used, it is fitted into the metal tube of the centrifuge by means of a bored cork. If a capillary has to be centrifuged, it is placed in the glass centrifuge cone provided with the centrifuge. Micro-centrifuge cones of sizes down to 0·5 ml. or less are desirable.

Wash bottles and cylinders.—The best wash bottles are of Pyrex glass with a capacity of 150 to 250 ml. The head of the flask has a standard female ground-glass joint, forming an outside glass-connection with the neck, thus preventing contamination of the wash liquid with dust. The two parts of the wash bottle are held together by wire springs attached to glass hooks fused to the head and neck of the flask. The delivery tube extends nearly to the bottom of the flask and its nozzle is drawn out to a capillary. The mouthpiece has a saliva trap.

If the amount of wash liquid has to be measured, a graduated wash cylinder (Pyrex) of 50 ml. capacity and with graduations in 1 ml. is useful. This wash cylinder is also fitted with an external ground-glass joint and mouthpiece with saliva trap.

Pipettes.—For introducing or transferring liquid samples or reagents, micro-pipettes are prepared when needed. Soft glass tubing of 4 to 5 mm. internal diameter is held in the flame of a batswing burner. When it softens it is removed from the flame and with a rotatory movement drawn out to a capillary of about 1 mm. bore. When cool, it is cut off and the end is drawn in a micro-burner to a finer capillary of 0·3 mm. bore. The finished pipette should be about 10 cm. long and taper down to about 1 mm. external diameter. To prevent the sample being contaminated with fragments of glass, the end is fire-polished by holding it momentarily in a small fine flame while blowing air through it so that the walls do not collapse.

Precision pipettes calibrated for 0·1, 0·2, 0·5 and 1 ml. are marketed.

BURETTES

Micro-burette.—The micro-burette has a capacity of 10 ml. and is calibrated in 0·05 or 0·02 ml. A magnifying lens is a useful adjunct to enable the reading of the meniscus of the solution in the burette to be made with ease. The markings on the burette should extend round or nearly round the circumference of the stem of the burette to enable errors of parallax to be minimised. The micro-burette as usually sold is of the automatic type with an internal delivery tube at the top which fills the burette automatically to the zero mark, any excess being siphoned back to the reservoir at the base of the burette. A tube attached to a side-arm at the top of the burette may be filled with soda lime to prevent access of carbon dioxide from the air to the

solution within the burette. The solution in the reservoir, with which the burette stem makes a ground-joint connection, is pumped into the burette by means of a small metal or rubber bellows. Between the bellows and the inlet tube for the compressed air to the reservoir is interposed a glass safety tube filled with soda lime and a glass T-piece with its side arm open. This side arm is closed with the finger while pumping the solution into the burette and is again opened when the solution has passed the zero mark on the burette to enable the siphon on the burette to operate and withdraw the excess liquid from above the zero mark of the burette. The burette and bottle are best cleaned by washing them repeatedly with cleaning solution (concentrated sulphuric acid saturated with potassium dichromate), then with a soap solution containing ammonia and finally rinsing them well with distilled water. Before being filled the burette should be rinsed twice with the solution it is to contain.

Weight burette.—The weight of titrant used in a titration may be determined much more accurately than the volume. Moreover, the errors inherent in the volumetric burette, which become of some importance in micro-analysis, are removed if the amount of titrant used is weighed. These errors result from changes of the temperature of the burette during the titration and such factors as parallax errors in reading the volumetric burette, errors in reading due to the drainage of the solution down the burette and adhesion of the solution to the walls of the burette above the liquid level. Though weighing the amount of titrant would appear to rob the titration of some of its simplicity and speed, very little is lost of these features in practice, for it is unnecessary to weigh beyond the second place.

Several types of weight burette are available. The usual type of weight burette, which consists of a straight-sided bulb of about 50 ml. capacity, with a tap below it, is convenient. Such a burette can be made very simply from a straight-sided separation funnel by drawing out the tube beneath the tap to a fine jet.

Whatever the type of weight burette used, the discharge tip should be coated thinly with paraffin wax to reduce the size of drops that it will deliver. To coat it, the tip is dipped beneath the surface of the molten wax. To prevent the wax choking the tip while it is still molten, a thin wire may be inserted into the capillary tip or a stream of air may be kept passing through the tip until the wax solidifies. Only a film of the wax is necessary on the tip.

The analyst should make an effort, when the titration is nearing its end, to split the drops delivered by touching the drop that forms on the burette tip to the inner surface of the vessel in which the titration is being made before the drop has grown to such a size that it becomes detached of itself from the burette tip. The split drop left on the

inner wall of the titration vessel is, of course, at once washed down into the body of liquid in the vessel, and the behaviour of the indicator observed.

Crucible tongs.—Crucible tongs 6 and 10 inches long are required for work in the high-temperature muffle. If they are to be used for handling platinum utensils they should be platinum-tipped or of stainless steel.

Glass rods with platinum wire hooks.—Glass rods or capillary tubing with platinum hooks sealed into the end are required for introducing platinum boats into and removing them from combustion tubes. The rods or tubing should be 20, 30, 40 and 60 cm. long. The hooks are of platinum about 0·5 mm. diameter and about 4 cm. long bent at the end to give a hook about 3 mm. long. They are best sealed into capillary tubing of about 4 mm. external diameter by means of a lead-glass seal. The diameter of the capillary tubing at one end is enlarged either by softening it in the blowpipe flame and splaying it out by means of a triangular metal tool or, preferably, by sealing it in the blowpipe flame and then blowing out the seal while still soft until the glass bursts. A blob of the stick of lead glass is fused on the platinum wire near one end of it in the blowpipe, the blob inserted into the splayed end of the capillary tube and the lead glass sealed to the glass capillary by heating the two in the pointed flame of the blowpipe, the flame being chiefly directed upon the blob of lead glass.

Dust filter.—If it is necessary to dry such tubes as a combustion tube or a filter stick in a current of air, the air must be made dust-free by filtering it through a filter tube. This is quite simply made by sealing a 5 cm. length of 1 cm. glass tubing to a capillary about 3 cm. long and filling the 1 cm. tubing with glass, or better, cotton wool. A rubber stopper of suitable size is placed on the capillary end of the filter in order to insert it into the mouth of the combustion tube or the filter stick before the air is drawn through it.

Rubber tubing.—Aged or impregnated tubing is required for certain connections in combustion trains. This can be bought. The analyst may prepare it himself as follows, though the preparation is hardly worth his time. The rubber tubing is placed in a flask with molten vaseline or paraffin wax and kept heated while suction and pressure are alternatively applied to the flask. This process is continued until the pores of the tubing are filled with the wax. The wax in the bore of the tubing after this impregnation is cleaned out by pushing a piece of cotton wool moistened with benzene through it and drying the bore with a second piece of cotton wool, left dry, pushed through the bore. The impregnated tubing bought on the market has to be cleaned in the same way.

CHAPTER IV

FILTRATION

SEVERAL systems of filtration for micro-analysis have been described in the literature. The two most commonly used—gravity filtration and the Emich inverted filtration using a filter-stick—are described below. The use of the filter-stick requires least skill and holds least possibility of error. In the other methods of filtration, the precipitate has to be transferred quantitatively to the filtering surface and great care has to be exercised, as it has in filtering precipitates on the macro-scale, to ensure that all the precipitate has been transferred. In the Emich filtration, the beaker in which the precipitation is done and the filter are weighed together; there is no need to ensure the complete transference of the precipitate to the filtering surface, the filter simply functioning as a method of separating the mother liquor from the precipitate.

A. PREGL GRAVITY FILTRATION

In this system the precipitate is transferred from the vessel in which it is formed to the filtering surface of a " filter-tube " in which it is washed, dried and weighed.

Filter tubes.—Two types of filter tube are available for the filtration, the one having a bulb-shaped constriction which contains an asbestos filter mat to retain the precipitate, the other (Fig. 5), which is the more convenient, having a coarse sintered glass plate to support the filter mat. The first type has a constriction below the bulb to allow the filter mat to be retained in it. The preparation of the filter mat is similar in both. The filter tube is put on the filtration apparatus and a layer of fine crucible asbestos filtered into the bulb or on to the sintered glass plate from a suspension of the asbestos in dilute sulphuric acid. If the first type is used, the filter mat should fill the bulb part of the stem. If the second type is used, the mat should be about 2 mm. thick. The asbestos is pressed down evenly, with a sharp-edged glass rod, until it is of the necessary thickness. The asbestos mat is washed first with 250 ml. distilled water, several times with hot cleaning solution (p. 32) and again with distilled water and alcohol. Its orifice is closed with a dust filter and the tube is dried with slight suction in the drying block at about 120° C. The filter tube is counterpoised with a glass tare bottle and lead or glass shot.

FIG. 5.

Filtration apparatus (Fig. 6).—The apparatus consists of a suction flask of about 250 ml. capacity provided with a one-holed rubber stopper. Through the stopper passes an adjustable glass sleeve 8 cm. long and 8 mm. internal diameter. The sleeve has a perforated rubber stopper through which the filter tube is inserted during the filtration. The solution and precipitate are siphoned from the test tube by means of a glass tube of 3 mm. internal diameter, bent as shown. The long vertical arm is 25 cm. long and bent at about 80°; the siphon then extends for a length of 10 cm., and is then bent at a wide angle so that the short arm, which is 6 cm. long, is parallel to the other.

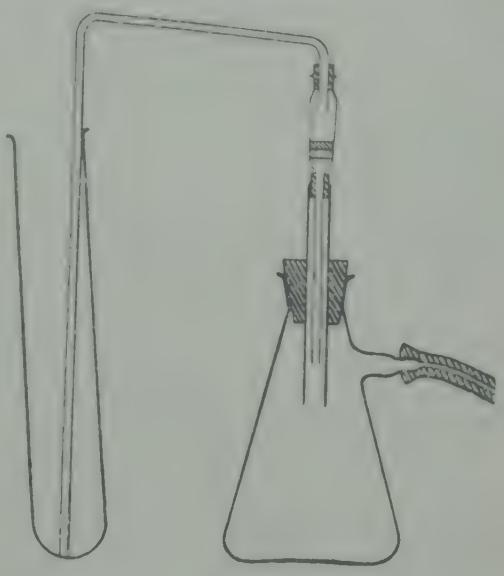

FIG. 6.

Method of filtering a precipitate.—The filter tube with its mat is treated in the same way before the analysis as after completing the filtration. It is put on the filtration apparatus and washed several times with the wash liquid to be used for washing the precipitate. Then it is removed from the apparatus, its outside wiped with clean chamois, the dust filter inserted and the filter tube connected to the suction pump with a flexible rubber tube which has a T-glass tube in the centre. A short rubber tube with a screw clamp is attached to the vertical limb to facilitate gradual reduction of the suction. The bulb of the filter tube is placed in the wider groove of the drying block and heated for 5 minutes at about 120° C. Then the shaft of the filter tube is placed in the narrow groove and moved up after 2 to 3 minutes to dry the remaining part. To cool the filter tube it is placed on a clean surface and the suction continued for 3 to 4 minutes. The suction is gradually broken by opening the screw clamp on the T-tube to avoid a sudden back pressure which may remove part of the asbestos mat. Finally, while held in a vertical position, it is wiped once with a moist flannel and three times with a dry chamois.

The filter tube is placed on a metal rack under a glass cover for 15 minutes before it is transferred to the wire support on the left pan of the balance by means of the wire fork. It is left there for 5 minutes with the side doors of the balance open and is then weighed. For a new filter the procedure of washing, drying and wiping has to be repeated until an agreement within 0·02 mg. with the previous weighing is obtained. The zero reading must be determined after

each weighing and corrections must be made for any deviation from it.

Before the filtration of a precipitate, the siphon of the filtration apparatus is washed with hot cleaning solution (p. 32) and rinsed with distilled water and alcohol. Its short arm is inserted through a good rubber stopper, which is also rinsed with a few drops of alcohol and the filter tube attached to the filtration apparatus as shown in the figure. The liquid and precipitate are quantitatively transferred from the precipitation vessel to the asbestos mat of the filter tube, with the filtration apparatus connected to the suction pump, by means of the rubber tubing provided with the T-tube. The speed of the filtration is regulated by means of the screw clamp on the vertical arm of the T-tube; the liquid should drip upon the filter mat at a rate of 1 or 2 drops per second. The bulb of the filter tube should never be filled completely; before this occurs the long arm of the siphon should be raised in the vessel until the liquid in the bulb of the filter tube has been drawn off. The bulk of the precipitate is siphoned off last. Then the vessel is rinsed with suitable wash liquid by spraying the wash liquid upon the wall while the vessel is rotated. Any particles clinging to the wall are loosened with a snipe feather, the vessel washed once more with alcohol, and the loosened precipitate transferred to the filter mat as before.

At the end of filtration, the rubber stopper of the siphon, with the glass tube protruding from it, is removed and rinsed with alcohol. The filter tube is filled to the edge with wash liquid and then with alcohol. When all the alcohol has been filtered off, the filter tube is dried, cooled, wiped and weighed as described above.

The tube may be used for successive filtrations without further treatment until the precipitate which has collected on the asbestos mat unduly impedes the filtration. The filter tube should be then cleaned and provided with a new mat.

B. EMICH INVERTED FILTRATION

Container and immersion filter.—The immersion filter (filter-stick) is weighed with the vessel which contains the solution and precipitate. This vessel and the filter-stick are of glass, if the precipitate needs only to be dried at low temperatures before weighing it, as in the case of silver halides. If the precipitate has to be ignited before it is weighed the container is a porcelain crucible and the filter stick of porcelain with a porous porcelain filter disc. (The porcelain filter may, of course, be used even if the precipitate only needs to be dried.) The porcelain filter-stick is available commercially. The glass filter-stick is also on the market but is easily blown by an analyst of small experience in glass-blowing. The head of the filter is of tubing 4 mm. internal

diameter and 2 cm. long. The handle is of capillary tubing of 2 mm. internal diameter and about ½ mm. wall. The tube should be of soft or Jena glass, not Pyrex, which retains electrical charges. The handle tube is constricted at the point where it joins the head to retain the asbestos filter mat that has to be placed in the head. The filter mat, about 3 mm. thick and of fine asbestos fibre, is deposited in the tube in the same way as described for the filter tube. The tube as a whole is washed in the way described for the filter tube before use (p. 34). The porcelain filter-stick is already provided with a filtering surface and needs only to be cleaned before it is used.

The beaker should be about 30 ml. in capacity. The crucible for the porcelain filter-stick should preferably be black inside, especially if the precipitate is white.

Preparation of glass beaker and filter-stick.—The glass filter-stick in its beaker is first cleaned by means of hot cleaning solution (p. 32). The cleaning solution is placed in the beaker and then the filter-stick inserted in it so that the solution penetrates the asbestos mat, and the whole is heated for 5 minutes on the water bath. The beaker is then rinsed with hot water and the filter washed with suction as described under *Treatment of the Precipitate* below. It is finally cleaned with hot concentrated hydrochloric acid and water in the same way.

After cleaning, the stick and beaker together are dried at about 120° C. in a drying oven while covered with a beaker of suitable size. The door of the oven should be left open until the water drops left on the filter-stick and beaker have evaporated. The heating is continued a further 10 minutes with the door closed. The stick and beaker are then withdrawn, wiped first with a damp cloth and then three times with chamois leather and placed near the balance-case. After allowing them to stand for 10 minutes, they are placed on the balance-pan and the side doors of the balance-case are left open. After 5 minutes, the doors are closed and the beaker and filter stick are weighed against a counterpoise of lead shot in a glass flask.

Preparation of porcelain crucible and filter-stick.—To bring the porcelain crucible and filter-stick to constant weight, they have to be treated in the following manner before a determination is made. The crucible is cleaned of precipitate from the previous analysis, well rinsed with distilled water and the exterior wiped with a clean cloth. A new filter-stick is cleaned by attaching the stem to the suction pump, immersing the plate in dilute hydrochloric acid solution and siphoning about 50 ml. of the solution through it. A used immersion filter is cleaned by brushing the precipitate from the porous filter plate and siphoning distilled water through it in both directions. Washing with hot concentrated acid should be resorted to only in extreme cases. The filter-stick is disconnected from the suction pump, its stem wiped

with a clean cloth and put in the crucible which is also wiped on the outside. The filter-stick remains in the crucible throughout the whole of the drying or igniting, cooling and weighing. After washing, the crucible is handled only with crucible tongs. If the precipitate from the determination is to be dried only before its estimation, the crucible, with the immersion filter in it head down, is transferred to a drying oven and dried in the same way as the glass filter-stick and beaker (p. 37). If the precipitate is to be ignited, the crucible and filter-stick within it are first dried at 120° C. in an oven and then placed within a muffle heated to no higher temperature than 1100° C. for 10 minutes. The crucible should be supported upon a silica plate within the muffle during its heating. After allowing it to cool for 15 minutes in the desiccator, it is transferred to the balance-pan and is weighed after 5 minutes against a counterpoise of lead shot in a glass flask.

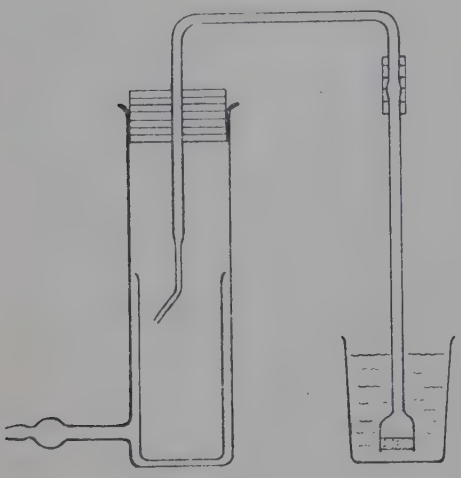

FIG. 7.

Filtration apparatus (Fig. 7).—The suction vessel is a flat-bottomed glass tube, 12 cm. long and 4 cm. in diameter, having a tubulure at the bottom, by which it is connected by rubber tubing to the suction pump. A glass T-piece is inserted in the line, its open limb being closed by rubber tubing with a screw clamp to enable the speed of filtration to be regulated. A specimen-tube of suitable size is placed inside the suction vessel to collect the filtrate. The siphon is a capillary glass tube of 5 mm. external diameter and 1 mm. bore. The arm which extends through the rubber stopper of the suction vessel is 9 cm. long and ends in an oblique capillary tip; above the rubber stopper it is bent at right angles to continue horizontally for 7 cm. and then it is bent again to form a vertical arm 5 cm. long which is also drawn out to a capillary tip. The filter-stick is connected to this tip with a short piece of flexible rubber tubing and extends into the porcelain crucible.

Precipitation.—As a rule, the amount of solution which has to be precipitated should not fill the porcelain crucible. If it does, the solution is transferred in small amounts at a time to the porcelain crucible, sufficient being poured into it each time so that the crucible is no more than three-quarters full. Each filling is evaporated to a small bulk on the water bath. (If more than three-quarters of the crucible is filled with solution, the solution may creep over the rim when it is being evaporated and material be lost.)

When all the solution has been transferred to the crucible and reduced to a suitable small volume, the precipitant is added to it drop by drop under the specified conditions for the precipitation. When precipitation is complete, the porcelain crucible is placed on a clean glass surface, covered with a beaker and, if it has been heated during the precipitation, allowed to cool.

Filtration.—The cleaned specimen tube is put in the suction vessel, and the rubber stopper carrying the siphon is inserted. After attaching the stem of the filter-stick to the capillary tip of the siphon, its filter mat (glass stick) or filter plate (porcelain stick) is moistened with a drop of distilled water and immersed in the solution in the beaker or crucible. Sufficient suction is applied so that the solution filters at a rate of 1 to 2 drops per second. After filtration, the precipitate in the container is washed three times with 1 ml. of wash liquid by spraying the wash liquid on the filter-stick and the wall of the crucible while rotating it. This solution is also filtered through the filter-stick as before. Then, without removing it from the crucible, the filter-stick is detached from the capillary end of the siphon and put into the beaker or crucible, where it remains during the whole process of heating or igniting and weighing.

If the glass filter-stick and beaker are used, they are dried together in an air oven under a beaker with the precautions given above. After drying, they are brought out of the oven, and allowed to remain for 10 minutes near the balance-case. They are wiped first with moist flannel and then successively with 2 pieces of chamois leather until clean, that is to say, until the leather slides over them smoothly. They are then placed on the left pan of the balance by means of crucible tongs, left for 10 minutes and weighed.

The porcelain filter-stick and crucible are dried like the glass filter-stick and beaker if the precipitate is to be dried before weighing it, or, if the precipitate is to be ignited before its final estimation, they are first dried at 120° C. in an oven and then heated to a suitable temperature in a muffle. The muffle temperature should not exceed 1100° C.; otherwise, precipitate may be lost through sputtering.

After drying or ignition, the crucible with its stick is withdrawn from the oven or muffle and left for 10 minutes upon a clay triangle. After a further cooling for 30 minutes in a desiccator, it is cleaned and dried like the glass filter, transferred to the balance-pan and, after 5 minutes, weighed.

Beakers and crucibles used in this work should never be left to stand unprotected on the bench, but should be placed under a large glass beaker resting on a clean glass plate or porcelain tile. Beakers, crucibles and filter-sticks are conveniently stored in a wooden block having a row of holes for the containers and, behind them on the block,

a corresponding set of smaller holes, drilled in the block to incline backwards, for holding the filter-sticks with their heads upwards. These blocks are taken to the balance for weighing the beakers and filter-sticks, and the weighed beakers and filter-sticks put in corresponding holes in the block immediately after weighing. In this way, many samples may be weighed out at the same time without the danger of later interchanging the sticks.

CHAPTER V

DETERMINATION OF MOISTURE, ASH AND METALS

A. DETERMINATION OF MOISTURE

In the analysis of hygroscopic materials, it is necessary to estimate their moisture content in order to correct their analysis for it, or at least, if the knowledge of the moisture content is of no importance, to dry the material and weigh it while in the dried state. The moisture content is determined by weighing the material in a boat in a weighing pig, transferring the material and the boat to the tube of a regenerating block, where it is heated at a suitable temperature in a current of inert gas until dry, replacing it in the pig and re-weighing it. The method cannot, of course, be used for materials which are volatile on heating.

Method.—A weighing pig is cleaned by means of moist flannel followed by chamois leather, a platinum-micro boat placed inside it and transferred to the balance-case. After it is cleaned, the pig should be handled only with chamois-clothed fingers. After 15 minutes, it is weighed by the method of swings to the usual accuracy. The pig is removed from the balance, the platinum boat withdrawn from it, about 20 mg. of material placed in it, the boat replaced in the pig, which is returned to the balance-pan and re-weighed after 5 minutes. The difference in weight gives the weight of material taken for the determination.

The pig is taken to a glass plate placed near the regenerating block (p. 30), opened, and the platinum boat transferred to the glass tube of the regenerating block. The boat is pushed down the tube to the capillary tube closing it, this part of the tube containing the boat having been kept out of the heating block. The end of the tube holding the boat is closed with a rubber stopper through which passes a capillary tube connected to a source of dry nitrogen (for example, a cylinder of nitrogen, the gas being passed through a wash bottle of sulphuric acid and a tube of anhydrone before entering the drying tube). The nitrogen is passed at a rate of about 1 to 2 bubbles per second through an ordinary wash bottle and the part of the tube holding the boat pushed to lie within the regenerating block. The heating block is heated to a suitable temperature; in general, one of about 110° C. (It should not be high enough, of course, to cause any appreciable volatilisation of the material.) After about 15 minutes the boat is withdrawn from the heating tube by means of a platinum hook on a glass rod and transferred by means of the platinum-tipped forceps to the weighing pig, which is at once closed. The pig is trans-

ferred to the balance-case. After 5 minutes, it is opened for a moment, to restore the air pressure within it to atmospheric, closed and re-weighed. It is advisable to repeat the heating, this time for 5 to 10 minutes to determine whether the material has come to the constant weight which shows that drying is complete. If necessary, the heating should be repeated until a constant weight has been obtained. If within a reasonable time, say, half an hour, a constant weight is not obtained, the analyst may well suspect the volatility of the material itself.

Calculation.—The moisture content is given by:

$$\text{Moisture} = 100 \times \frac{\text{loss in weight, mg.}}{\text{weight of sample, mg.}}$$

B. DETERMINATION OF ASH AND METALS

Metals in organic compounds and their ash contents are determined by burning the substance in air and weighing the residue as metal, oxide, sulphate or "ash." Most metals are determined as sulphates by incineration with sulphuric acid. The following are determined as oxides, usually after addition of nitric acid: aluminium, copper, iron, magnesium.

APPARATUS

Micro-muffle.—The micro-muffle (Fig. 8) consists of two tubes of resistant glass, preferably Jena glass. One is a horizontal tube about

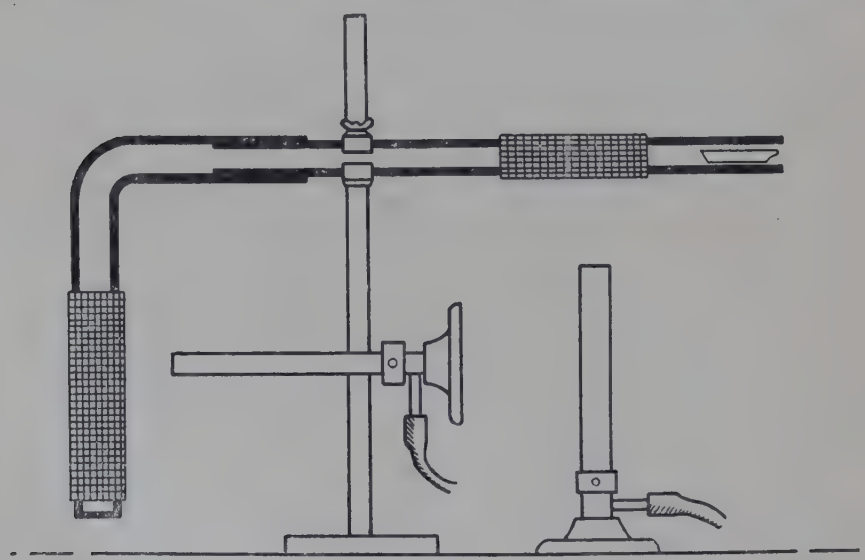

FIG. 8.

20 cm. long and 1 cm. in diameter. The other is a bent tube, one arm of which, about 3 cm. long, slides over one end of the horizontal tube

for a distance of about 4 cm., while the other arm, about 10 cm. long, hangs vertically. The bent tube should make a fairly loose fitting with the horizontal tube. Asbestos paper is wound round that part of the horizontal tube surrounded by the bent tube so that the two tubes make a close fit. Bunsen flames, playing on wire gauze round each of the tubes at the positions shown, are used for heating the tubes. The hot vertical tube thus supplies a current of hot air for the combustion.

A platinum or porcelain boat may be used to contain the material to be burnt. It is placed at the end of the horizontal tube for the combustion.

Platinum sheath for the boat.—The boat for the material is surrounded by a platinum cylinder to retain any material that might otherwise be lost by sputtering or frothing during the combustion. This sheath is made from platinum foil, about 0·04 mm. thick, 3 cm. long and with a diameter of 0·9 cm. or slightly less than the diameter of the horizontal combustion tube. A platinum wire fused to the end of the cylinder and bent in a loop is an advantage for handling it.

REAGENTS

Dilute sulphuric acid.—A 20 per cent. solution of the concentrated acid in distilled water.

Dilute nitric acid.—A 50 per cent. solution of the concentrated acid in water.

METHOD

About 20 mg. of the substance are weighed accurately into the combustion boat previously cleaned by boiling it in dilute nitric acid and burning off in the bunsen flame. Two or three drops of dilute sulphuric or nitric acid are added to the material in the boat from a capillary pipette while the boat rests on a clean glass surface. The boat is inserted into the platinum sheath, which has also been previously cleaned like the boat, and the two placed together just inside the mouth of the horizontal combustion tube so that only the hook on the sheath protrudes from the tube. The heating of the horizontal tube is begun with the flame fully on and about 5 cm. from the boat. The bunsen-burner heating the vertical part of the wider combustion tube is also turned on and adjusted so that its flame is about 5 cm. high and heats the wire gauze round the tube at a point about half-way along its length. This burner remains stationary throughout the combustion, but that on the horizontal tube is gradually taken towards the boat, at about a centimetre in each step until it reaches the boat in 5 to 10 minutes.

When the material ceases to fume, the bunsen flame is turned fully on under the boat and heating continued for a further 15 minutes. The boat and platinum sheath are then removed from the tube together by means of the metal forceps, held in the outer cone of the non-luminous bunsen flame until they glow and placed on the block in the micro-desiccator. After 5 minutes the boat is re-weighed. If the residue is incompletely burnt, as shown by the presence of black particles in it, the combustion is repeated after adding another drop of acid. Before re-introducing the boat and sheath prior to the combustion, the combustion tube should have been allowed to cool.

The determination may be made without the platinum sheath, but as extreme care may be necessary to prevent creeping of the material and loss by sputtering, the sheath should be used.

The ash content of a material is determined in the above manner but without the addition of sulphuric or nitric acid before the incineration.

CHAPTER VI

DETERMINATION OF CARBON AND HYDROGEN

Semi-micro and micro-methods of determining the carbon and hydrogen contents of organic materials are usually modifications of Liebig's method of burning the substance in a current of oxygen and collecting the carbon dioxide and water from the combustion in appropriate absorbents. From the increase in weights of the absorbents during the combustion, the weights of the two elements can be determined. As, in general, the organic material may contain halogens, sulphur and nitrogen, all of which give rise to acid gases during the combustion, provision has to be made in the combustion apparatus for the absorption of these elements or their oxides before the stream of gas enters the absorption train, so that they will not interfere with the determination by being taken up by the absorbents.

We describe Ingram's method (3) for the semi-micro determination of these elements with some modifications, chiefly in the scavenging train, which is used to purify the oxygen supplied to the combustion tube. There is, of course, no reason why Ingram's method should not be used in its entirety, but the apparatus we describe has some merits in its simplicity and the ease with which it can be manipulated.

A description is also given of the Bobranski-Sucharda (1) method of automatically controlling the combustion.

Mention may be made of two methods which enable the combustion of compounds containing more unusual elements, such as arsenic and antimony, to be made accurately. Ingram (18) has given a modification of his method described here, which enables compounds containing arsenic, antimony and halogens to be analysed satisfactorily. Kirner (19) has described a filling of the combustion tube for coping with compounds containing phosphorus, bismuth, tin and arsenic.

APPARATUS

The assembly is shown in Fig. 9. Oxygen is fed into the combustion train either from a cylinder of the compressed gas, fitted, for ease of adjustment of the flow, with a reducing valve, or from a large gas-holder. The oxygen first passes through a pre-heater, containing platinised asbestos heated to about 550° C. to burn any carbonaceous material that the oxygen may contain and which would otherwise be burnt in the combustion tube and appear in the analysis. The hot oxygen is cooled in the lower part of the pre-heater before it passes through rubber tubing having a screw-clamp upon it to regulate the

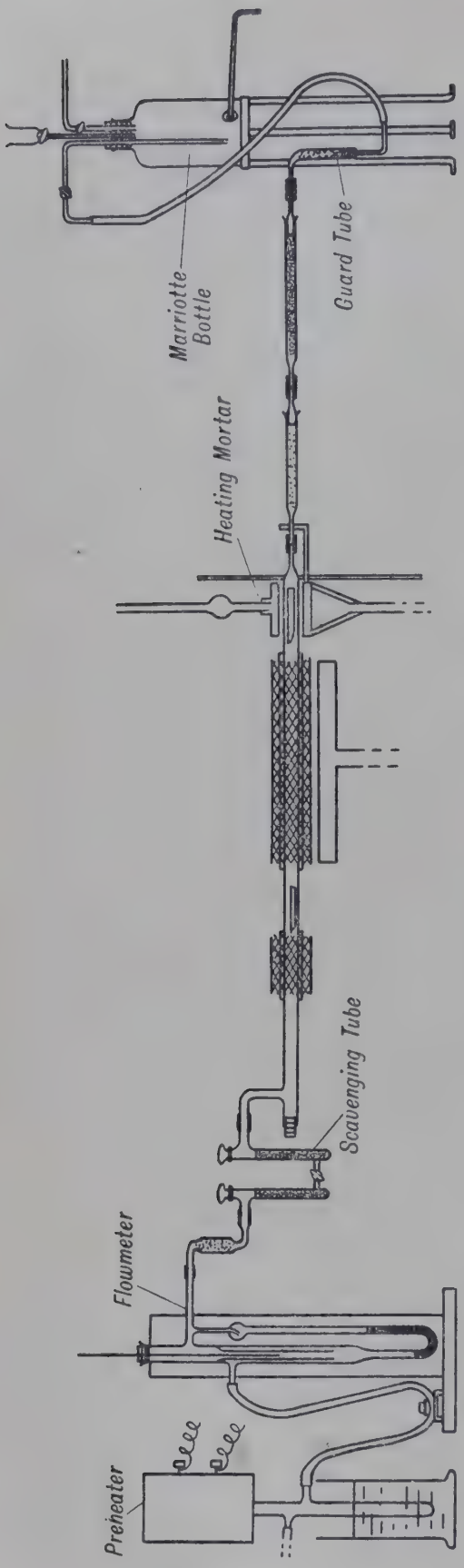

FIG. 9.—ASSEMBLED APPARATUS FOR THE DETERMINATION OF CARBON AND HYDROGEN

flow of gas into the flowmete
where its speed is measure
On leaving the flowmeter, th
oxygen is purified by passin
it first through a short tub
containing the desiccant, an
hydrone, and then through
U-tube containing in the firs
limb soda asbestos to absor
carbon dioxide and, in th
second limb, the desiccan
anhydrone. The side arm o
the U-tube, through which th
oxygen leaves, is fitted with
the rubber tubing which con
nects it to the side arm of the
combustion tube. The com-
bustion tube is supported on
a combustion stand. The
middle part of the combustion
tube which holds the catalyst
for ensuring that the combus-
tion is complete is heated by
the long burner. The boat
nearer the inlet end of the
combustion tube contains the
material to be analysed and
the material is burnt off by
means of a movable bunsen-
burner. The gases from the
combustion, other than car-
bon dioxide and water, are
absorbed in lead peroxide
which is placed in a boat near
the outlet end of the combus-
tion tube. The lead peroxide
is kept at a temperature of
about 190° by means of a
heating mortar which contains
boiling dekalin. The gases
issuing from the combustion
tube first pass through an
absorption tube which con-
tains the anhydrone to absorb
the water vapour in them, and

then through an absorption tube which contains soda asbestos for absorbing the carbon dioxide. The second absorption tube is connected through a drying guard tube, to a Mariotte bottle which exerts a suction effect on the train through the fall of water from it and so helps in maintaining the correct conditions of pressure of the oxygen within the combustion train. This bottle also affords a convenient means for detecting any abnormalities that may occur during the combustion.

CONTROL OF OXYGEN FLOW AND SCAVENGING TRAIN

Oxygen supply.—The oxygen may be supplied either from a cylinder of the compressed gas, fitted with a reducing valve to permit easy adjustment of the flow of gas in the train, or from a gas-holder in which the gas is stored over water. Instead of having the usual large reservoir top, the gas-holder may be fitted simply with a glass tube having two side arms, one near the top, the other near the bottom; the lower side arm is an inlet for a stream of water from the tap, the upper the outlet for the stream of water. This form of head is less top-heavy than the common type and reduces the variation in pressure of the oxygen in the holder as it is expelled during the combustion.

Pre-heater.—Commercial oxygen from a cylinder of the compressed gas contains some carbonaceous material, for example, in the form of oil from the valve connections on the cylinder. (Some organic material may also be picked up from the rubber tubing through which the gas flows if tubing of inferior quality is used. The pre-heater should therefore be joined to the flowmeter by aged tubing. In other connections in the train the glass tubes to be connected should abut on one another as described later.) The amount of organic material in the oxygen is normally sufficient to cause an appreciable error in the micro-combustion but not in the semi-micro method. Though its removal is not, as a rule, essential in the latter method, it is desirable that some form of pre-heater should be used to remove it. The oxygen from the oxygen supply flows directly to the pre-heater. The simplest form of pre-heater is the White-Wright type (20) shown in Fig. 10. It is made of Pyrex, or preferably silica, of the dimensions shown and has two internal tubes, one in the top half and the other in the bottom half, making annuli with the outer jacket. One side arm leads in the oxygen so that it first flows upward through the upper annulus which is filled with platinised asbestos, descends through the inner tube to the bottom, then passes through the annulus of the lower half of the tube and finally out of the pre-heater through the second side arm which is connected with the lower annulus. The platinised asbestos in the upper half of the pre-heater is heated to about 550° C. by means of a small tubular furnace which surrounds the outer glass tube of the

pre-heater above the entry side arm. The bottom half is cooled by means of a beaker of cold water.

The small furnace for heating the pre-heater may be simply made by winding No. 26 nichrome wire on an alundum tube 2 to 2·5 cm. in internal diameter and 30 cm. long. (None of these specifications need be rigidly adhered to.) The spirals of the wire on the alundum tube should be about 3 mm. apart. The spiral may be kept in place by twisting the lengths of wire left at either end on the end spirals, while the spiral as a whole is kept in place by plastering alundum cement on it and allowing the cement to harden. A cylinder of sheet tin, 8 to 10 cm. wide and the same length as the alundum tube is closed at the top and bottom with discs of uralite sheeting. The disc at the lower end of the furnace has a central hole through which the pre-heater tube may be inserted. The other disc closes the upper end of the furnace completely. The annular space between the alundum tube and the outer tin cylinder is filled with a heat-resistant filling such as magnesia or kieselguhr. The ends of the heating wire may be connected separately to the two leads from the transformer (if alternating current is the source of electricity) or may be connected to a socket inserted into the side of the outer cylinder of the furnace, a plug connected to the wires from the source of electric supply completing

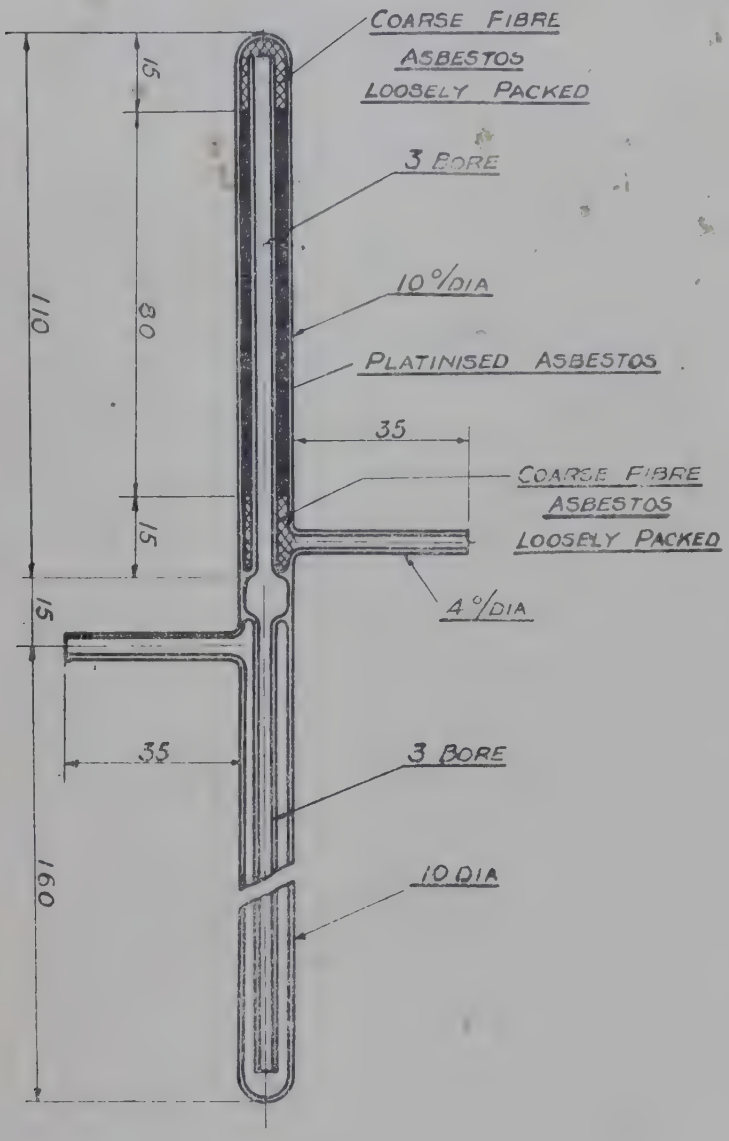

FIG. 10.

he connections of the heating wire to the source of electricity. The oltage supplied to the furnace is adjusted so that the pre-heater tube s heated to a temperature of approximately 550° C.

Precision pinch-cock.—The pre-heater is attached to the flowmeter which follows it in the train by means of narrow, matured rubber ubing. To enable the flow of oxygen to be closely regulated, a Pregl precision screw-clamp is placed over it at a suitable point. For convenience the screw-clamp is pinned to the board to which is attached the flowmeter, the clamp being placed near to the inlet tube of the flowmeter.

Flowmeter.—Any suitable flowmeter may be used for measuring the flow of oxygen. That shown in the diagram of the train and in Fig. 11 is a modified form of the White-Wright flowmeter (20), which enables the capillary orifice throttling the flow to be easily adjusted to give a suitable head of water on the manometer in order to measure it. The flowmeter is a combination of capillary orifice and manometer. It consists of a narrow U-tube, 3 mm. internal diameter; one arm—that on the inlet side—is widened and contains an inner narrow tube making an internal joint with it. A glass rod passes down this inner tube and it is this internal tube and the glass rod which constitute the variable capillary orifice. The capillary may be changed over a wide range by adjusting the position of the glass rod in the internal tube. The top of this arm of the U-tube is closed by a small rubber stopper through which the glass rod passes. A trace of glycerine in the hole of the rubber stopper is useful for lubricating the glass rod where it passes through the stopper.

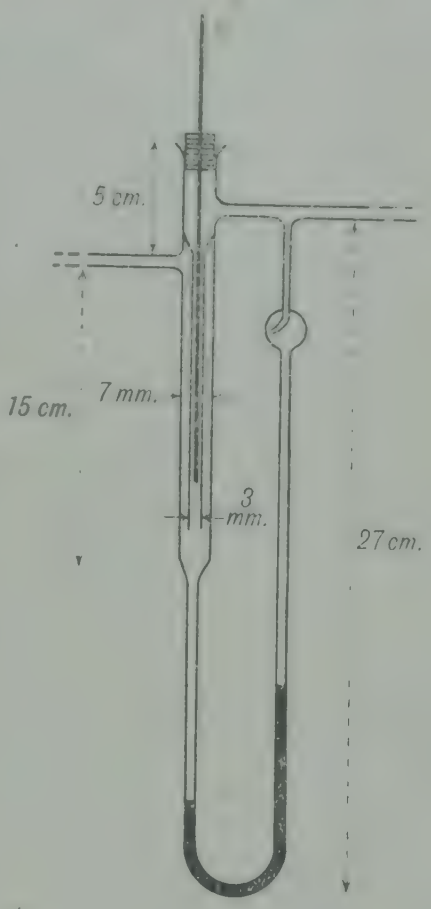

Fig. 11.

The narrow part of the U-tube contains water, preferably coloured, for example, with eosin, to enable the position of its menisci to be read easily. Side arms are provided for the inlet and outlet of the oxygen through the flowmeter. The oxygen, it will be seen, enters through the side arm, passes down the annulus between the wide part of the U-tube and its internal tube, up through the capillary orifice and thence out of the flowmeter through the side arm. The flowmeter is conveniently

attached to a wooden stand on which is pasted a piece of graph-paper or other scale behind the manometer part of the flowmeter.

There may occasionally be irregularities in the control of the gas flow due to hysteresis effects of the rubber tubing and the liquid may be blown out of the manometer. The small splash head incorporated in the manometer tube minimises this nuisance.

The flowmeter may be calibrated by means of the Mariotte bottle.

Purification U-tube.—The flowmeter is directly attached to a U-tube or preferably attached to it through a short piece of 1-cm. glass tubing. The piece of glass tubing contains anhydrone, held in place in the tube by means of plugs of cotton wool. The placing of desiccant at this point has the merit of reducing the rate of exhaustion of the purifying reagents in the U-tube. The U-tube is filled, in the arm on the inlet side, with soda asbestos to absorb carbon dioxide in the oxygen, and on the outlet side with anhydrone to complete the drying of the gas. If an ordinary U-tube is used, the two reagents are separated by means of a plug of cotton wool at the bottom of the bend of the tube and the columns of the two reagents are kept in place by cotton plugs on top of them. It is of great advantage, in order to minimise exhaustion of the soda asbestos, to use the Friedrich U-tube which is illustrated in the diagram. This has a glass tap at the base. By keeping the tap closed when the apparatus is not in use, the two reagents are kept separate. If they are not kept separate, there is an exchange of water vapour between them which is shown in the fairly rapid exhaustion of the soda asbestos at the base of its column at the part near the column of anhydrone.

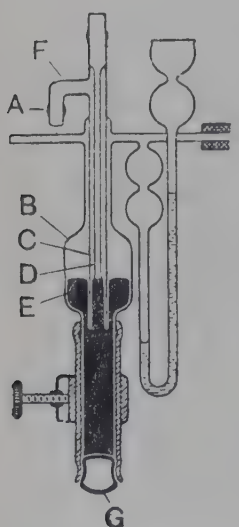

FIG. 12.

The outlet side arm of the purifying U-tube has on it the short piece of rubber tubing (3 cm. long, 2 mm. bore, 1 mm. wall thickness) which fits into the inlet side arm of the combustion tube so that the U-tube may be directly attached to the combustion tube.

Bobranski-Sucharda regulator for the oxygen supply.—The Bobranski-Sucharda regulator (Fig. 12) automatically regulates the combustion of the material in the combustion tube. By taking advantage of the changes of pressure in the tube during the combustion it correspondingly alters the supply of gas to the burner used to burn the substance. One essential for the satisfactory combustion of the material is that there should be an excess of oxygen in the gases flowing through the combustion tube throughout the combustion. The regulator ensures that this excess is maintained. The regulator is a pressure-thermo-regulator, pro-

ided with a manometer tube, A. The reservoir, B, and connecting ube C, are filled with mercury up to the gas inlet tube, D, at E. is the gas-outlet tube. The regulator lies between the precision crew-clamp in the scavenging train and the purifying U-tube, and replaces the flowmeter described above. A piece of heavy, wide ubber tubing is joined to the bottom of the reservoir and is closed by heavy glass rod. A pinch-cock on this piece of rubber tubing enables he level of the mercury in the reservoir to be altered. Any increase in pressure in the combustion tube resulting from too rapid combustion of the material depresses the surface of the mercury in the reservoir, and raises the level in tube C. The gas fed to the burner from the combustion flows through the tube D sealed within tube C; the rise in level of the mercury within these tubes caused by the increase in pressure thus cuts off the supply of gas or at least reduces it. When combustion has slackened somewhat, the pressure in the combustion tube falls and the end of the gas-inlet tube in the regulator is uncovered so that more gas is fed to the combustion burner to accelerate the combustion. In this way, the speed of combustion of the material is automatically regulated according to the pressure in the tube. In order that the combustion should require no attention, the combustion burner is placed beneath the combustion boat throughout the determination. (In the method we describe, the combustion is started with the burner some distance from the combustion boat and the burner is gradually taken up to it.)

Before use the apparatus is cleaned and dried. The manometer is filled to the zero mark with coloured water. The apparatus is inserted in the train, and while the taps on the train are open the reservoir is filled with mercury through the gas inlet tube to within about 4 mm. of the end of this tube. The connections to the gas supply and the combustion burner are made and the burner lit. The precision screw-clamp on the train is closed, the oxygen supply to the combustion tube turned on and the precision screw-clamp gradually opened until the manometer shows a pressure of 6 cm. of water. If, now, the screw-clip on the rubber tubing on the reservoir of the regulator is fully opened, the flame on the burner should be about 5 cm. high; and by fully closing the screw-clip it should be possible to extinguish the burner. If these conditions are not fulfilled, the amount of mercury in the reservoir should be adjusted until they are.

Combustion tube.—The combustion tube consists of a hard glass tube (Jena Supremax glass) or silica tube 57 cm. long and 1 to 1·2 cm. internal diameter. One end is drawn out to a snout 3 cm. long and 3 mm. in diameter. At a distance of 4 cm. from the other end, the mouth, is a side arm bent at right-angles, as shown, which serves as the inlet for the stream of oxygen to the tube. The outlet end of the

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U-tube which completes the scavenging train is attached to this side arm by means of the rubber tubing, on the U-tube of the scavenging train, so as to make a glass-to-glass contact.

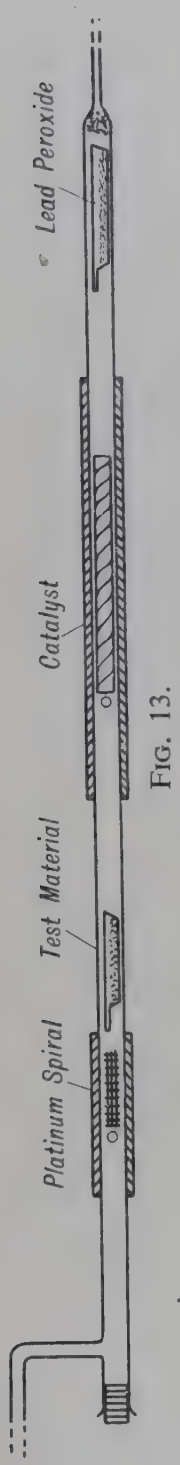

FIG. 13.

Before use, the combustion tube is cleaned by immersing it in a warm mixture of potassium dichromate—concentrated sulphuric acid cleaning solution contained in a long glass tube, or by pouring the cleaning mixture down it, leaving the tube wet with cleaning mixture overnight. The tube is then successively washed with tap water, distilled water and acetone. It is dried by attaching one end of it to a suction pump, the other end being closed by a dust filter (p. 33) so that only dust-free air is drawn through it. The drying may be expedited by warming the tube near the inlet end by means of a bunsen flame so that warm air is used for the drying.

Filling for combustion tube (Fig. 13).—The filling material for the combustion tube is a mixture of copper oxide, lead chromate and, as catalyst, ceric oxide. Lead peroxide is used for absorbing the nitrogen oxides which may be given off during the combustion of the material.

The mixture of copper oxide and lead chromate is one of equal parts of the two components. The copper oxide is the ordinary wire form lightly ground before use and sieved, that part passing the 10-mesh (B.S.I.) sieve being used for the purpose. The lead chromate is also ground before use. For the mixing, it is sufficient to shake the two components well together.

The preparation of the ceric oxide catalyst, the ceric oxide being dispersed over pumice, is described under *Reagents* below. The copper oxide-lead chromate mixture and ceric oxide are supported within the tube in a roll of copper gauze. The roll of gauze is prepared by forming a cylinder of pure copper gauze from a piece of the gauze measuring 16 cm. long and 4 cm. wide. The gauze is wrapped round a glass rod 4 to 5 mm. in diameter, so that a cylinder of gauze 16 cm. long and about 5 mm. in diameter is formed. One end is pinched to close it and through this end is threaded a piece of platinum wire which is bent into a hook; the hook makes it easy to withdraw the gauze from the combustion tube. The ceric oxide-pumice is then poured into the roll to form a layer 5 cm. long in the gauze cylinder and the rest of the tube is filled with the copper oxide-lead chromate mixture. The filling is

kept in the roll by means of a wad of ignited asbestos wool. It is essential that the external diameter of the roll should be about 2 mm. less than the internal diameter of the combustion tube so that free space to this extent is left in that part of the combustion tube occupied by the roll. If the roll fits too tightly into the combustion tube, low carbon figures may result.

The lead peroxide is placed in a porcelain boat about 4 cm. long and of such a width as to fit snugly into the combustion tube. The boat is cleaned by boiling with concentrated nitric acid, washing with distilled water and finally heating it strongly for 5 minutes. After allowing it to cool, 2·5 gm. of lead peroxide are filled into that end of the boat to be placed nearer the snout of the combustion tube. Any particles of the peroxide are brushed from the outside of the boat before it is inserted into the combustion tube. This amount of lead peroxide lasts about 15 combustions, after which it must be renewed.

The clean, dry combustion tube is filled as follows : A small wad of asbestos is ignited by holding it in the flame of a bunsen-burner for a few minutes by means of metal forceps so that the whole of it glows. This asbestos is then pushed by means of a long, clean glass rod to the snout end of the combustion tube. It is tapped gently by means of the rod to keep it in place ; the tapping should be gentle so that this plug does not too greatly choke the oxygen flow during the combustion. Any loose fibres of asbestos left along the length of the tube are withdrawn from the tube by pushing down it a loose plug of cotton wool and then withdrawing it by means of a platinum wire hook fused into a long glass rod. In withdrawing the cotton wool, the loose asbestos fibres should be drawn out of the tube with it. The boat of lead peroxide is next inserted into the tube. It is placed in the mouth of the tube by means of forceps and then pushed to the snout end of the tube so as to lie against the plug of asbestos wool at that end. It is essential that while pushing the boat into the tube no particles of the peroxide fall from it into the tube. If any do fall on to the wall, they should be carefully brushed out by means of a wad of cotton wool. In handling the tube or in attaching the scavenging train to it, care should be taken not to rotate the tube ; otherwise, peroxide will fall from the boat. If it does, the tube should be cleaned and refilled.

The copper gauze cylinder containing the copper oxide-lead chromate mixture and ceric oxide is now inserted into the tube, the open end, that containing the mixture, being inserted first. The cylinder is pushed down the tube into such a position that it lies centrally with respect to the length of the long burner heating that part of the tube containing it. Finally, a roll of silver gauze 3 cm. long and nearly 1 cm. diameter is pushed down the tube to lie against the copper gauze roll. This roll is made by wrapping silver wire repeatedly round a thin metal rod until a roll of the required dimensions is obtained.

Support for the combustion tube and heating arrangement.—The combustion tube is supported on a combustion stand which has been described earlier (p. 30). The catalyst in the tube is heated by means of a long burner (p. 29) and the lead peroxide by means of a heating mortar.

The combustion tube is placed on the combustion stand in such a position that the snout end overhangs the stand by approximately 9 cm. The long burner is placed under the tube so that it heats the combustion tube up to the end of the combustion stand. The position of the copper gauze containing the catalyst in the combustion tube should be such that it is placed centrally in the tube with respect to the long burner. In order that this part of the tube, heated by the long burner, should be heated fairly uniformly round its circumference, the tube is surrounded by an easily-fitting brass tube the same length as the long burner and placed directly over this burner. The burner heats this sheath directly and the height of its flame should be so adjusted that it is about 1·5 cm. high and heats most of the circumference of the brass sheath round the combustion tube. The brass tube should then be at a very dull red heat. The height of the burner and its flame should be adjusted until this condition is fulfilled.

The part of the tube containing the boat of lead peroxide is heated by means of a heating mortar containing dekalin so that the peroxide is kept at a constant temperature of 190° C., the temperature at which is absorbs nitrogen oxides most efficiently. The most suitable type of heating mortar is the Schobel, which, being of glass, allows observation of the peroxide in the tube. The mortar consists of a cylindrical glass annulus, the inner tube being such that the combustion tube slides into it fairly easily. One end of this inner tube is restricted: it allows the snout end of the combustion tube to pass, but is sufficiently narrow to prevent the main body of the combustion tube from passing through it. The annulus of the mortar is filled with dekalin to a height sufficient to submerge the upper surface of the internal tube: the combustion tube is thus, so to speak, completely surrounded by the liquid. A wide glass tube, connected with the annulus containing the dekalin, rises from the body of the mortar and serves as an air condenser for the dekalin boiling within the mortar. The body of the mortar is heated by means of a micro-burner fixed to the base of the mortar. This base supports the body of the mortar. In the Schobel mortar, a metal plate makes a close fit with the bottom surface of the glass body of the mortar; this plate is heated directly by the micro-burner and transmits the heat to the dekalin. The flame of the burner should be adjusted to such a height that the dekalin boils gently.

A copper rod with flattened end is provided with the mortar. This rod is loosely fixed in a sleeve running the length of the mortar and is heated by it. The flattened end is placed over the inlet end of the

water-absorption tube connected to the snout end of the combustion tube and so serves to drive water, condensed at this end of the absorption tube, to the absorbent within the body of the tube.

It is advisable to fix the combustion tube firmly in the mortar by wrapping asbestos paper round that part of it which lies within the mortar before inserting it therein. That part of the asbestos paper on the upper surface of the combustion tube should be cut away to allow uninterrupted view of the boat of lead peroxide in the tube through the glass walls of the mortar.

The material to be analysed is burnt off in the combustion tube by means of an ordinary bunsen flame. A bunsen, placed near the inlet end of the combustion tube, should be provided for this purpose. A short piece of brass tubing about 5 cm. long and fitting loosely over the tube is placed round the combustion tube at the point where the flame of the combustion bunsen-burner heats it.

Fig. 14.

Absorption tubes (Fig. 14).—Because the accuracy of a carbon and hydrogen analysis depends largely on the constant weight attainable by the absorption tubes, their construction and dimensions, especially those of the capillary, are of the greatest importance. The water absorption tube is about 16 cm. long overall. The filling chamber has a diameter of 8 to 9 mm. and is about 8 cm. long; it is separated from the adjoining air chamber by a thin glass wall with an aperture of 0·2 to 0·25 mm. The absorption tube ends in a capillary tubing about 3 cm. long and 3·3 to 3·5 mm. external diameter or the same diameter as specified for the capillary ending of the combustion tube. This capillary tubing of the absorption tube has two constrictions, each being 5 mm. long and having an inner diameter of 0·2 to 0·25 mm.; the two constrictions are separated from one another by an air chamber 3 mm. long and 2 to 2·5 mm. internal diameter. This design of the capillary ends reduces the diffusion of atmospheric vapours, especially moisture, into the tube, thus contributing to the constancy of weight attainable by the absorption tube. The head or open part of the absorption tube has a ground-glass joint provided with a hollow ground-glass stopper which has an aperture of 0·2 to 0·25 mm. in diameter at its curved base; its opposite end is drawn out to a capillary tubing of the same construction and dimensions as the end of the absorption tube.

The carbon dioxide absorption tube is the same in construction and

dimensions as the water absorption tube, except that it has a somewhat longer filling chamber, 9 to 9·5 cm. long.

Filling the absorption tubes: water absorption tube.—The water absorption tube is cleaned by washing it with distilled water and alcohol and is dried on the suction pump or in a drying oven at 120° C. Sufficient cotton wool is placed against the glass wall at the end of the filling chamber to form a fairly compact layer 3 to 4 mm. long. This cotton wad prevents the clogging of the aperture of the glass wall by particles of the desiccant. A 1·5 to 2 cm. layer of coarse anhydrone (magnesium perchlorate) is then introduced, followed by another 3 to 4 mm. loose layer of cotton wool. The rest of the tube is filled within 5 mm. of the ground-glass joint with fine but not powdered anhydrone. Another cotton wad, occupying the remaining 5 mm. space in the absorption tube, completes the filling. The ground-glass stopper is carefully warmed outside the flame of a micro-burner, and a little Krönig's glass cement is applied to the warm surface of the stopper, which is then quickly inserted and rotated in the ground-glass joint of the absorption tube; a transparent seal should be obtained. If insufficient cement has been applied the ground-glass joint is carefully warmed outside the flame with constant turning until the cement softens and the stopper can be removed. More cement is then applied and the sealing repeated. The excess cement is removed from the rim of the ground-glass joint by rubbing it with a tuft of cotton wool moistened with benzene.

Carbon dioxide absorption tube.—After the carbon dioxide absorption tube is cleaned as described above for the water absorption tube, a cotton wad 4 to 5 mm. long, then a layer of 2 to 3 cm. of anhydrone (fine) are introduced, followed by a loose layer of cotton wool 3 to 4 mm. long. The rest of the tube is filled with soda asbestos to within 5 mm. of the ground-glass joint. Another layer of cotton wool is added and the tube sealed as described above.

Counterpoising the absorption tubes.—Absorption tubes may be counterpoised with open tare bottles containing lead shot and distinguished from each other by letters or numbers, such as H for the anhydrone tube and C for the carbon dioxide tube. This counterpoise is satisfactory when the changes in the laboratory air in temperature and pressure are small. However, lead shot tends to take up moisture and a tare bottle with ground-glass stopper is better. Glass beads may also be used, when a larger tare bottle is necessary.

Mariotte bottle guard tube.—The safety tube, which lies between the absorption tubes on the combustion tube and the Mariotte bottle, absorbs any moisture that might pass from the Mariotte bottle to the

absorption tubes. The tube is about 10 cm. long and 1 to 1·2 cm. in diameter. It is open at one end and has an air chamber at the other which terminates in a right-angle capillary about 3 cm. long and 4 mm. external diameter. The tube is filled with anhydrone and a fairly tight layer of cotton wool is placed before and after the filling. The open end is closed with a rubber stopper through which a right-angled capillary is inserted. A rubber tube about 60 cm. long is attached to the capillary of the anhydrone tube of the Mariotte flask connecting it to the glass tube inserted through the rubber stopper on top of the Mariotte flask.

Mariotte bottle.—The Marriotte flask supplies sufficient suction to the combustion train to overcome the resistance offered by the absorption tubes, so that approximately atmospheric pressure prevails at the rubber connection between the capillary end of the combustion tube and the water absorption tube. This equilibrium of pressure with atmospheric conditions at this point is important to prevent either loss of combustion gases due to their absorption by the rubber connection in case of excess pressure, or introduction of moisture from the air in case of reduced pressure. The bottle may be 1 or 2 litres in capacity, preferably the larger because it allows of eight determinations being made without refilling it. A glass tube or side arm is fixed into the lower tubulure of the bottle by means of a perforated cork stopper, an arrangement which allows of easy adjustment. The side arm should have a length equal to the height of the bottle; it has an external diameter of about 3 mm. and a bore of 2 mm. It is bent at right angles at the end which is inserted into the cork to form a limb 3 to 4 cm. long. The other end is bent so as to be vertical to the horizontal side arm and drawn out to a capillary tip of 1 to 1·5 mm. bore and 1·5 to 2 cm. length. The neck of the bottle has a 3-hole rubber stopper. A glass tube of about 2 mm. bore bent twice at right angles and carrying a tap between the bends is inserted through one opening to extend almost to the bottom of the flask. This tube is connected by rubber tubing to the guard tube. The second opening in the rubber stopper is provided with a 2-way tap to allow egress of air when filling the bottle from the tap funnel which passes through the third hole. The bottle is supported on a suitable stand such as a long-legged tripod so that a 250 ml. graduated cylinder, in which the actual displacement of water by the oxygen during the combustion is measured, can be placed under the horizontal side arm.

Treatment of absorption tubes.—After the absorption tubes are assembled, sealed and cleaned of the superfluous cement round their ground joints, they are tested for their resistance and their gas-tightness. For testing their gas-tightness they are inserted in the correct manner into the combustion apparatus and tested along with the rest of the

apparatus for leaks in the manner described below. The two absorption tubes are always connected together head to tail.* The other end of the water-absorption tube is connected to the snout end of the combustion tube, and the corresponding end of the tube for absorbing carbon dioxide to the guard tube of the Mariotte bottle. Their resistance is tested by inserting them into the combustion train, lowering the side arm of the Mariotte bottle and opening the tap on the gas inlet of the Mariotte bottle in order to draw air through the absorption tubes by means of the suction given by the Mariotte bottle. The bottle should be filled to a depth of 20 cm. of water. The effective head of the suction is thus about 22 cm. of water. Under these conditions, with the inlet tap of the Mariotte bottle fully open, it should be possible to draw at least 10 ml. of air per minute through the absorption tubes. If this speed is not attained, each absorption tube should be tested separately to determine which of the two or whether both offer too much resistance to the flow. (When one tube alone is tested, it should, of course, be possible to draw double the specified amount through it.) Care should be taken that the bore of the tap on the Mariotte bottle inlet is sufficiently wide, not only for this test, but for the combustion also. It should be at least 2 mm. in bore, as we have described earlier.

With the resistance and air-tightness of the tubes tested, they are ready for the preliminary weighing tests described below. The analyst inexperienced in this analysis should pursue the routine described until his schedule agrees with that stipulated.

Wiping and weighing the absorption tubes.—The weights of water and carbon dioxide resulting from the combustion of the organic material in the combustion tube are determined by the difference in weights of the two tubes before and after the combustion. Fouling of the tubes in handling them during the combustion may cause perceptible errors in the estimated increases in their weights. Hence, before the tubes are weighed, either before or after the combustion, they must be brought to the same condition in their cleanness. This is done by adopting the technique of cleaning first suggested by Ostwald, which consists in cleaning them first by means of moist flannel cloth and then wiping them dry by means of chamois leather. The technique of cleaning to be described should be followed scrupulously. The analyst should follow the tests described to assure himself that his technique is satisfactory.

Micro-analysts differ a little in their technique of cleaning. Through habit, we follow the Pregl technique, but the others differ little, even in detail, from it. What is essential is that once the technique has

* If either tube is accidentally reversed for a test, the analysis should be discontinued and the tube refilled.

been decided on, it should invariably be followed in detail. A further essential is that the time schedule given should also be followed.

The anhydrone tube is always wiped and cleaned first. When this has been done, the soda asbestos tube is cleaned similarly. As each tube is cleaned it is put on the rack support for the absorption tubes to await its weighing. The cleaning of the two tubes takes about 3 minutes. The zero point of the balance is then determined and the anhydrone tube placed on its wire support on the balance-pan. After a few minutes, the weighing is begun and it should be completed in exactly 10 minutes after taking the tubes from the combustion train. The soda asbestos tube is substituted for the anhydrone tube on the balance and its weighing is completed exactly 5 minutes later, that is to say, 15 minutes from taking the tubes from the combustion train. When once the anhydrone tube is cleaned, it begins to gain, or rather apparently to gain, in weight as it gradually comes to temperature equilibrium with the balance-case. This equilibrium is attained within 10 minutes, after which any change in weight becomes very slow. Too long a time cannot be allowed to elapse before the anhydrone tube is weighed because it is weighed full of oxygen and changes in weight will be caused later by gradual displacement of the oxygen in the tube by air from outside it. This time schedule, therefore, should be strictly adhered to.

The cleaning of the tubes is done as follows : For this purpose a pair of moist pieces of flannel and two pairs of chamois leather are required (all about 12 cms. square). The moist pieces of flannel are folded double and placed over the tube so that the folds meet at the middle of the tube. Each piece is grasped near its fold, the one in the left hand, the other in the right, the grasp being chiefly by the thumb below the tube and the first finger on top of the tube. Each piece of flannel is given a rotary motion round the tube, and the flannels are gradually withdrawn towards the end of the tube while the rotary motion is being imparted to them. The rotary motions of the two flannels will, of course, be in opposite directions. The rotary motion is continued until the fingers on the fold reach the ends of the capillaries at the ends of the tubes. Naturally, the bare fingers will never touch the glass of the tube. While holding the tube in the left hand by means of the moist flannel, the other moist flannel is put back in its dish and one of the first pair of dry clean chamois leathers taken up in the right hand, folded and wrapped round the absorption tube so that its fold is at the centre of the tube. The other moist flannel is then discarded, the second of the first pair of chamois leathers folded by the left hand and wrapped round the absorption tube so that the fold is at the centre of the absorption tube against the fold of the first. The tube is then wiped with these two chamois leathers in the same way as with the moist flannels, with a rotary motion and gradually

withdrawing them in opposite directions to the ends of the tube. When this wiping has been completed, the chamois in the right hand is put back into its container and the first of a second pair of chamois leathers is taken up from its vessel. The second of the first pair of chamois leathers is discarded and the second of the second pair folded round the absorption tube. The tube is then wiped with the second pair exactly as with the first pair. After cleaning the tube in this manner, the leather should glide over the tube without any apparent friction. The clean tube is finally put in its rack. The rack is placed either on the top of the balance-case or beside the balance ; if the table top supporting the balance is of stone, a cardboard sheet should separate the rack from the table. The carbon dioxide tube is then wiped similarly and placed on the rack.

The tubes on the rack are placed near the balance in order to come to temperature equilibrium with it. While this equilibrium is being attained, the zero point of the balance is determined. (The zero point of the balance should always be determined before weighing the absorption tubes, since about an hour elapses between successive weighings of them, before and after combustion. As it happens, the shift in zero point of the analytical balance is rarely appreciable and this precaution is usually unnecessary. But as it is the invariable rule in micro-analysis, the analyst would do well to get into the habit of doing it.)

The water absorption tube is replaced by the soda asbestos tube, which is weighed in a similar manner ; this weighing is completed in exactly 5 minutes after the weighing of the water absorption tube.

The inexperienced analyst would do well to re-weigh the tubes at once, as quickly as possible, without adopting a rigid time schedule, to verify the first two weighings. These re-weighings should agree within the limits of experimental error of the balance with the first weighings. With experience, these duplicate weighings become unnecessary.

The absorption tubes should be weighed in the same order, the water-absorption tube first. It may be difficult to attain constancy of weight at times owing to an accumulation of electrostatic charges on the absorption tubes. To dissipate such electrostatic charges the two ends of the absorption tubes are touched simultaneously with a metal wire.

Blank tests on absorption tubes.—It is necessary for the analyst to be sure that he can reproduce the weight of the absorption tubes (within the usual error of $\pm 0{\cdot}05$ mg.) after they are rewiped. In the combustion, the tubes are weighed while filled with oxygen. For the present purpose, we follow Niederl's test (31, p. 102), in which they are weighed filled with air for practice in the technique.

After the absorption tubes have been filled and cleaned of their superfluous cement, they are connected together glass-to-glass and head to tail by means of cleaned, impregnated rubber tubing. The free end of the carbon dioxide absorption tube is connected to the guard tube of a Mariotte bottle. If the rubber connections stick too tightly to the absorption tubes they are lubricated with a trace of glycerine applied to a cotton-wool tuft wound round knurled iron wire. All excess glycerine is removed by wiping out the bore with a dry cotton-wool tuft. The free end of the water-absorption tube is connected to a scavenging train consisting of a long tube (30 by 1 cm.) packed with anhydrone and soda asbestos. A bubbler containing sulphuric acid is attached to the other end of this tube. The delivery tube of the bottle is lowered until a delivery of 10 ml. of water per minute is obtained. 150 ml. of scavenged air are passed through the absorption tubes, after which the tap on the inlet tube of the Mariotte bottle is closed and the absorption tubes disconnected from the bottles. The rubber connections on the absorption tubes are removed and put in a desiccator containing calcium chloride. The two absorption tubes are cleaned, first the water absorption tube, then the carbon dioxide tube, and wiped and weighed in the manner described above.

The experiment of passing dry air is repeated, 150 ml. of air being passed and the tubes re-cleaned and re-weighed. The second result should be within 0·05 mg. of the first weighing before passing the 150 ml. of dry air. If the difference exceeds this, the experiment must be repeated until the correct technique of wiping and weighing the tubes has been acquired.*

REAGENTS AND MATERIALS

The reagents used should be of micro-analytical (" M.A.R.") grade.

Anhydrone (magnesium perchlorate).—The anhydrone should be sifted upon the 60-mesh (B.S.I.) sieve to remove any powdered material. The coarse size, which is marketed, is also required.

Asbestos.—Gooch crucible asbestos is used for the asbestos plugs in the combustion tube. It is ignited before use, either by heating for about half an hour at about 900° C. or by holding small amounts of it with the platinum-tipped forceps in the flame of a bunsen-burner.

Asbestos, platinised.—About 1 gm. of short-fibre asbestos is first purified by boiling it in dilute nitric acid and then igniting it at red heat. 1 gm. of chlorplatinic acid is dissolved in a few ml. of distilled water or 0·5–1 gm. of scrap platinum dissolved in a few ml. of *aqua regia* by boiling. The purified asbestos is put in the platinum solution so that

* Niederl and Niederl always weigh the absorption tubes filled with air and use this method to displace oxygen prior to weighing. We only use it as an exercise to acquire the wiping and weighing technique.

it absorbs it. The platinum salt within the asbestos is reduced by adding to the mixture of solution and asbestos a few ml. of cold saturated sodium formate solution containing sufficient sodium carbonate to give it an alkaline reaction. The liquid is poured off and the platinised asbestos washed with distilled water to remove adhering salts. Finally the asbestos is dried in a beaker on the water-bath.

Ceric oxide.—The catalyst for the combustion is prepared thus. 16 gm. of ceric ammonium nitrate is dissolved by warming in 50 ml. of 1 : 1 nitric acid solution and hot pumice (previously ground to lie between the 35- and 60-mesh (B.S.I.) sieves) is added to the solution. The solution containing the pumice is allowed to cool, the solution poured off and the pumice, placed in a porcelain crucible, heated over a bunsen flame or in a muffle at about 700° C. until no more fumes of nitric acid are evolved.

Copper oxide : wire form.—The wire-form copper oxide is lightly crushed to particles about 3 to 4 mm. long and particles passing the 10-mesh (B.S.I.) sieve sifted from it. The coarse fraction is ignited in a porcelain crucible at about 900° for half an hour with occasional stirring. If it is ignited over a bunsen, the crucible containing the copper oxide is placed within a larger one supported on an asbestos plate containing a hole for insertion of the larger crucible ; the oxide is ignited with a strong flame for about an hour with occasional stirring.

Lead chromate.—The lead chromate is heated at a temperature of about 500° (not exceeding 550°) in an electric furnace with frequent stirring; the material should not be allowed to fuse.

For the oxidising filling of the combustion tube, equal parts of the above copper oxide and lead chromate are mixed just before introducing the mixture into the combustion tube.

Lead peroxide.—Only the purest form of lead peroxide gives satisfactory results. Though commercial lead peroxide can be purified by digestion with concentrated nitric acid, it is hardly worth the analyst's time to do so when the pure reagent is available on the market.

Silver gauze.—A plug of silver wire is bundled up to form a tuft about 2 cm. long.

Soda asbestos.

Krönig's glass cement.—This may be brought or prepared by melting together and mixing 1 part of white beeswax and 4 parts of resin and casting it into sticks about 10 cm. long and 1 cm. diameter.

Cleaning cloths.—For cleaning the absorption tubes before weighing, moist flannel and chamois leather is required. The pieces of flannel and leather are about 12 cm. square and are kept in roomy Petri dishes. The flannels are moistened before use. They should not be wet;

excess water must be removed by squeezing the flannels and pressing them between the folds of a towel. Four pieces of chamois are required. They should be of good grade of soft leather. They are washed, when washing is desirable, in lukewarm soapy water to which a few drops of ammonia have been added. They are rinsed thoroughly and dried at room temperature. They should never be cleaned with organic solvents.

Rubber tubings.—The rubber tubing from the oxygen reservoir to the pre-heater should be of good grade and about 7 mm. external and 5 mm. internal diameter. Impurities on the inner wall should be removed, but it is not necessary to age this tubing. The connections between pre-heater, scavenging train and combustion tube must be of seamless impregnated rubber tubing about 7 mm. external diameter and 2·5 mm. bore. The impregnated tubing can be bought. As bought, the bore still contains the wax with which the tubing has been impregnated. The bore is cleaned by passing through it a tuft of cotton wool moistened with a little benzene and then a dry tuft of cotton wool. The cleaned, impregnated rubber tubings are stored in a desiccator over anhydrone. It is desirable that the two rubber tubings for the absorption tubes should be placed in the same position for all analyses and they may be suitably marked with ink on their surface to enable this to be done.

METHOD

Assembling the combustion train.—A table of convenient height and suitable length (1 m. high, 2 m. long), which allows easy access to, and complete survey of, all parts of the apparatus, should be chosen as the basis of the complete apparatus. Depending on its size and the space available, the oxygen cylinder (if one is used instead of a gasholder) may be laid on the table or placed next to it, but so close that a length of rubber tubing, 30 to 40 cm. long, attached to the outlet of the reduction valve on the cylinder, is sufficient to connect it to the scavenging train.

Except for the combustion tube, all other parts of the apparatus should be ready for attachment. Such glass parts as pre-heater, anhydrone tubes etc. are cleaned and dried and filled as described above.

The scavenging train may be regarded almost as permanent equipment, for it needs little attention when once its parts have been filled and connected. The filling of the U-tube and anhydrone tube have been described. The connections of the different parts will be obvious from the diagram and needs little comment. The lubricant used for slipping the rubber tubing over the glass tubing of the different parts

of the scavenging train up to the pre-heater is glycerine. Beyond the pre-heater, no lubricant should be applied. The tubing leading from the pre-heater to the anhydrone tube should be as short as possible so that little organic material is taken up from the rubber by the stream of oxygen. If a combustion tube with a side arm is in use, this connection may almost be made glass-to-glass. If the combustion tube has no side arm the connection has to be a few cm. long to allow the scavenging tubes to be moved back 2 or 3 cm. when the boat containing the material to be analysed is being inserted.

The rubber tubing used for this part of the apparatus should be suited to the glass tubes over which it is slipped. It should be only 1 to 2 mm. smaller in internal bore than the glass tubing which it connects. Wider tubing fails to ensure a gas-tight joint while narrower rubber tubing becomes excessively stretched and leaks may soon develop. To ensure tight connections the rubber tubing should be pushed at least 1 cm. over the glass tubing.

The pre-heater furnace is supported by a stout retort clamp on a heavy retort stand at a suitable height, so that the bottom half of the pre-heater may be inserted in a beaker of water. The pre-heater needs no other means than the furnace to keep it upright if the furnace tube fits fairly closely (but never too closely) round the pre-heater. If the furnace tube is wide, it is of some assistance if the bottom of it has a stout asbestos board covering it with a central hole for the pre-heater tube. The asbestos board may be wired to the furnace exterior to keep it in place or supported on a tripod stand.

The flowmeter is attached to an upright wooden stand either by spring clamps or other suitable means.

The Friedrich U-tube for scavenging the inlet gases is supported on a small retort stand by means of wire. It is supported on the level of the inlet opening of the combustion tube so that the outlet arm of the U-tube can be connected easily to the side arm of the combustion tube. The drying tube between this U-tube and the flowmeter is bent into a Z-shape with right-angle bends so that it can make glass-to-glass connections with these tubes. This form of connection between the different parts of the scavenging train gives a reasonably stable assembly. A rather firmer scavenging train would be obtained by clipping all the parts on one upright wooden stand attached to a wide base.

All the rubber tubing, except that between the oxygen cylinder or gasholder and the pre-heater, should be of aged and impregnated type. Whenever the tubing on this part of the scavenging train has to be taken off it is best to cut the connections; after some time, the rubber sticks to the surface of the glass and to remove it other than by cutting may lead to breakages.

The long gas burner, combustion stand and the heating mortar are next assembled. The height of the heating mortar is adjusted so that

the combustion tube fits into the central passage but still rests on the V-shaped notches of the stand.

A strip of asbestos paper, 6 cm. long and 1·5 cm. wide, is placed in the central passage of the heating mortar, to fit round the combustion tube, and is cut away so as to allow some sight of the combustion tube within the glass heating mortar. A disc of asbestos board about 5 cm. square and 3 mm. thick, with a central hole slightly larger than the diameter of the combustion tube, is placed round this tube between the heating mortar and the combustion stand. The other end of the heating mortar which faces the absorption tubes has a similar disc of asbestos board and then an asbestos shield about 30 cm. high and 20 cm. wide, having an opening at the proper height to allow the capillary end of the combustion tube to pass through. This shield is necessary to protect the absorption tubes from the heat of the heating unit. It is kept in place by wiring it to the heating mortar. The long burner is placed under the stand and 3 cm. away from the heating mortar, so that this space of 3 cm. of the combustion tube is left unheated. The height of the long burner is so adjusted that the brass tube of the combustion tube is immersed in its flame and of sufficient intensity that this tube is heated to a dull red.

With the combustion tube in place, the two absorption tubes, always joined to one another head to tail, are attached, the anhydrone tube being connected directly to the combustion tube and the soda-asbestos tube to the guard tube of the Mariotte bottle. The absorption tubes are supported on micro-retort stands, the tubes lying in the bottom of the crook of the wires soldered to the cross arms of the stands. The rubber connections are made of aged, impregnated rubber tubing of 2 mm. internal and 4 mm. external diameter. The connections of the water-absorption tube to the capillary end of the combustion tube and to the soda-asbestos tube should be glass-to-glass. This is essential.

The Mariotte bottle is connected, by the glass tube passing through the rubber stopper on its neck, to its guard-tube using about 60 cm. of rubber tubing. With the bottom side arm of the Mariotte bottle horizontal and its tip over the 250 ml. graduated cylinder, the apparatus is complete.

It is essential, of course, that the apparatus should be free from leaks. The apparatus is tested for leaks before the combustion in a simple manner. A further indispensable condition is that the blank on the apparatus should be suitably low. The tests used to verify that these conditions have been established in the apparatus are described below.

Preliminary heating of the combustion tube.—A freshly-filled combustion tube must be heated for some time before it can be used. The pre-heating is carried out by attaching it to the apparatus, but leaving

its capillary end open and adjusting the oxygen flow to a delivery of 3 to 4 ml. per minute. The combustion tube is heated for about 3 hours with all the heating devices lighted. To restore the necessary moisture equilibrium of the lead peroxide after this heating, it is necessary to burn one or two unweighed samples, about 5 mg., of an organic substance (for example, benzoic acid). This procedure will prevent low hydrogen values, which would otherwise result in the first few analyses, because of the tendency of the lead peroxide to retain some moisture tenaciously much beyond the time period of a combustion. When not in use the combustion tube is closed by attaching the drying tube of the Mariotte flask to its capillary end ; it is always kept under pressure of oxygen to prevent atmospheric vapours, especially moisture, from entering the system. A combustion tube protected in this way will remain in good condition even after prolonged idleness and need only be heated for one or two hours before a determination is made.

Blank determination.—Any tendency of the absorption tubes to increase in weight when no material is burnt in the tube (a tendency which, of course, should be negligibly small in a correctly-assembled apparatus) may be due to several causes: improper filling of the absorption tubes and the tubes in the scavenging train, bad connections and poor rubber connections causing leakages and so on. The possible causes of the undue increase in weight may be eliminated one by one by testing the air-tightness of the tube, running a blank on the cold tube and running a blank on the fully-heated tube.

The improper filling of the absorption tubes will have been disclosed in the test described earlier (p. 61), in which air is passed through them.

For the blank tests, the absorption tubes are first filled with oxygen by connecting them in the combustion train. (The tubes might equally well be filled by direct attachment to the scavenging train, but with the combustion train fitted up, the present arrangement is as convenient and gives the inexperienced analyst some practice on the combustion train as a whole.) All the connections are made, except that the inlet end of the combustion tube is left open, and the oxygen flow is adjusted to 6 ml. per minute, as determined on the flowmeter. The inlet end of the combustion tube is then closed by its stopper. The tap on the inlet tube to the Mariotte is closed so that the oxygen flow will gradually come to rest. This tap is now opened, when water begins to flow from the side arm of the Mariotte bottle, this side arm having been brought to the horizontal position.

If this results in some variation in the oxygen flow as shown on the flowmeter, the side arm to the Mariotte may be slightly raised or lowered to correct it. The correct position of this side arm may remain unaltered throughout the use of the apparatus, the oxygen flow in subse-

quent tests being simply started by opening the tap on the Mariotte bottle.

The apparatus is, as always, first tested for leaks. With the oxygen flowing, the tap of the absorption tube on the scavenging train is closed when the flow of water from the Mariotte bottle should stop within a little time. If the flow does not stop, every connection should be gone over to trace the leak, making the test for leaks at every change.

With the tube remaining cold, 100 ml. of oxygen are passed, the time of flow being checked against the volume of water collected in the graduated cylinder beneath the Mariotte bottle. This check should always be made to ensure that the flowmeter is functioning correctly.

When this amount of oxygen has passed, the flow is stopped by closing the tap on the U-tube of the scavenging train and the guard tube on the Mariotte bottle is connected to the capillary end of the combustion tube to prevent entrance of moist air. The absorption tubes are cleaned and weighed in the usual way, the water-absorption tube being weighed 10 minutes after detachment from the combustion tube, the carbon dioxide absorption tube 5 minutes later.

The absorption tubes are replaced in the combustion train for the blank on the cold tube, which is essentially a repetition of the last experiment (whose only purpose, of course, was to fill the absorption tubes with oxygen). The train is again tested for leaks and 100 ml. of oxygen are passed in the way described above. The Mariotte bottle is then closed, the absorption tubes detached, cleaned and weighed. The difference in the two sets of weighings of the absorption tubes are the blanks on the cold combustion tube. The blank is satisfactory if the increase in weight of each of the absorption tubes is 0·1 mg. or less.

The blank on the heated combustion tube is carried out as follows: The pre-heater, long burner and burner for the heating mortar are lighted and the various temperatures allowed to come to their normal working level. The absorption tubes, filled with oxygen, are cleaned, weighed and connected into the combustion train, head to tail. (They may be used from the blank experiment on the cold tube if this experiment has immediately preceded the present blank experiment, their weights after that test being taken as the initial weights for the present test.) The rubber tube on the other end of the water-absorption tube is attached glass-to-glass with the capillary end of the combustion tube and the free end of the other absorption tube is joined to the guard tube of the Mariotte bottle. The rest of the apparatus is now connected and the oxygen flow begun. The inlet tap on the Mariotte bottle is opened and the flow of oxygen adjusted to 6 ml. per minute. 150 ml. of oxygen are passed at this rate, the water from the Mariotte bottle being collected in a 250 ml. graduated cylinder. The tap on the Mariotte bottle is then closed, the absorp-

tion tubes disconnected, the guard tube of the Mariotte bottle connected to the capillary outlet of the combustion tube and the absorption tubes cleaned and weighed in the usual manner. The increase in weights of the tubes should be 0·1 mg. or less.

If there is an undue blank in the test on the unheated apparatus, the fillings of the scavenging train are at fault. If this is so, these fillings must be renewed. If the blank is not noticeably increased in the test on the heated combustion tube, the combustion tube filling may be taken as efficient.

The troublesome part of the filling is the lead peroxide, especially for the hydrogen values, for it retains water when moisture-laden gases are passed over it, and then gives it off slowly over a prolonged period of time. The lead peroxide of a new filling of a combustion tube may give off traces of water even after several hours. It may also do so after the apparatus has lain idle for some time. This fault can be remedied by heating the apparatus for a few hours while passing oxygen through it at 6 ml. per minute. If high hydrogen values persist, a better sample of lead peroxide should be used for the filling. A high hydrogen blank may also result from the hygroscopic properties of the rubber connections between the water-absorption tube and the combustion tube. This can be detected by placing them in a desiccator for several hours over a desiccant before the blank determination is done ; as a rule, this drying should not be too rigorous, for otherwise the hydrogen value may tend to be low.

A high carbon dioxide blank should not be obtained. If it is, it can be attributed to excessive lubriction of the rubber tubings on the tube. The rubber connections should be re-made, taking care to use less glycerine for the lubrication. The blank test on the hot combustion may be then repeated.

As regards this lubrication, it may be noted at this point that the connection between the water-absorption tube and the combustion tube requires lubrication about every third determination owing to its proximity to the heating unit, while that between the two absorption tubes requires lubrication about every sixth determination.

METHOD OF ANALYSIS

Analysis of known substances.—After the blank determination has proved satisfactory, a pure substance such as benzoic acid, or azobenzene, is analysed. When correct results have been obtained (within 0·2 per cent. of the theoretical of the carbon and hydrogen) the apparatus is ready for analysing unknown compounds. The inexperienced analyst should analyse several compounds of known composition, both solids and liquids, with various elements in them.

PREPARATION OF THE SAMPLE

Solids and semi-solids.—Approximately 20 mg. of the substance are weighed accurately in a clean platinum boat (p. 24).

Liquids.—Liquids are weighed in weighing capillaries (p. 27); if they are inappreciably volatile they may be weighed into a platinum boat. The capillary, containing a little potassium chlorate, is filled with about 20 mg. of the liquid in the usual way. Before being introduced into the combustion tube, the capillary is centrifuged with the delivery tip uppermost, its tip broken off and both tip and capillary placed in a platinum boat for insertion into the combustion tube, with the open end innermost.

METHOD

Introduction of the sample.—With the apparatus connected together, the long burner and the burner in the mortar heating the tube to the correct temperature and the oxygen flowing, but with the tap on the Mariotte bottle closed, the cleaned and weighed absorption tubes are put in place. (The oxygen flow is maintained while the sample is inserted into the combustion tube in order to prevent ingress of air into the tube.) The rubber stopper of the combustion tube is taken out and, unless attached directly to the scavenging train, put on the top of the micro-desiccator. The micro-desiccator, with its top removed, is taken to the mouth of the combustion tube, the platinum boat holding the sample is taken from the copper disc in it, which is then on the level with the mouth of the combustion tube, and introduced into the mouth of the tube by means of clean, platinum-tipped forceps. It is pushed with a clean glass rod to within 5 cm. of the heating unit. Finally, the tube is closed tightly with the stopper.

Combustion.—The side arm of the Mariotte bottle is lowered to the horizontal position, its inlet tap opened and the displacement of water by the oxygen passing through the system measured and standardised to a flow of 6 ml. per minute. The combustion is started about 5 cm. in front of the platinum boat containing the sample with a non-luminous, slightly-hissing flame which extends about 2 cm. higher than the brass tube round the combustion tube which this burner heats. The burner is gradually moved towards the sample, at no more than 1 cm. at a time and preferably less, until there are signs that the heat is affecting the sample. The movement of the burner and its brass tube is interrupted while the behaviour of the sample is observed. It should be noted whether it distils, sublimes or chars. The burner should rest some moments in its present position, since the start of the combustion is one of the most crucial parts in the determination. The first decomposition of the sample should be as slow as possible, particularly if the hydrogen value of the sample is high. If the sub-

stance distils, it should be driven forward, when the movement of the burner is resumed, to form a drop of distillate between the platinum boat and the heating unit. It should not be allowed to condense near or in contact with the platinum boat; if it condenses in contact with the boat, difficulties will be created in the later heating; the heat may be transmitted so rapidly through the boat when the burner approaches it that the distillate in contact with it is too rapidly vaporised. If the material sublimes, a ring of sublimate is formed round the tube somewhat in advance of the brass tube heated by the burner; the aim of the analyst should be to drive this ring slowly forward without causing appreciable evaporation of it. If the material chars, the aim of the analyst should be to drive the tars forward like a sublimate ring, but as a rule it will be found that the heating has to be direct, with the brass tube over the tar, before it tends to disappear. Moreover, with chars, as with material containing inorganic elements, the direct heating of the boat directly should be prolonged to ensure complete decomposition.

Having taken care that the first decomposition of the material has been slow, the burner, with the metal heating tube round the combustion tube, is again moved forward slowly, at 0·5 cm. at a time or somewhat less. The evaporation of the drop of molten sample between the boat and heating unit should be so slow that its disappearance is only very gradual. Towards the end of the disappearance of the drop the burner may be moved a trifle more rapidly until it arrives at the boat. Less care is needed if the material has formed a ring of sublimate whose behaviour in the tube may be more easily followed and the burner may approach the boat at a more regular pace. Nevertheless, the combustion should not be too hurried. With chars, the disappearance of the tars from the decomposition of the material can be followed fairly easily and the boat approached by the burner at a fairly rapid pace. When the burner reaches the boat (which will require about 10 minutes), it is allowed to remain under it for 5 minutes or longer if the material has charred or if it contains inorganic material. After this time the burner is again moved forward, fairly rapidly, unless there is still much material left in the tube, when the advance of the burner should be appropriately slow. About 10 minutes will be required to reach the long burner.

The outflow of water from the Mariotte bottle should be observed at frequent intervals during the combustion. The flow should remain reasonably steady; any retardation in it will indicate too rapid combustion. If the flow becomes appreciably slower, the combustion should be interrupted until the flow of water resumes its normal speed.

No description of the method of combustion can cover all materials which the analyst is likely to meet. Experience with a wide variety of compounds is the best way of instilling confidence in him in undertaking the analysis of any material submitted to him.

When the burner for the combustion has reached the long burner and the whole of the material has been driven over into the filling, the combustion burner and its metal tubing are taken back to the position they had at the start and their path over the boat retraced up to the long burner. About 3 minutes will be required to reach the boat, the burner is kept under the boat about 2 minutes and another 3 minutes will be required to reach the long burner.

The combustion burner may now be turned out while the flow of oxygen is allowed to continue for about 20 minutes to sweep the combustion products out of the combustion tube into the absorption tubes.

During the combustion the copper-rod heater of the heating mortar will have been resting on the capillary inlet of the moisture-absorption tube. This end of the tube should be watched to see that it does not become choked with condensed water. If it does the fact will be observed in a retardation, if not cessation, of the flow of water from the Mariotte bottle. If so, the combustion should be interrupted by keeping the combustion burner stationary until by manipulating the copper rod the water has been driven into the body of the absorption tube.

It will probably be found, at the end of the combustion proper, that water has condensed in the empty chamber of the water-absorption tube. If so, it is desirable to heat this part of the absorption tube by laying the copper rod over it while the products of combustion are being swept out of the combustion tube; the condensate is thus vaporised and carried forward to the desiccant.

When the combustion products are swept out of the tube, the tap on the Mariotte bottle is closed and the absorption tubes are detached. If more combustions are to be made the oxygen supply is kept open to maintain an atmosphere of oxygen in the combustion tube. The absorption tubes are wiped, the zero point of the balance determined and the absorption tubes weighed according to the usual time schedule. The necessary corrections are made in the second weighing for any change in the zero point before calculating the weights of carbon and hydrogen appropriate to the increases in the weights of the absorption tubes.

At the end of a run of combustions, the burners are extinguished and the guard tube of the Mariotte bottle connected to the snout end of the combustion tube. The oxygen supply is kept open until the tube is cold so that before it is shut off the combustion tube is under pressure of oxygen. Thus air is unlikely to leak in before the apparatus is again used.

Calculation.—The weight of carbon in the material is 0·2727 times the increase in weight of the absorption tube for the carbon dioxide and the weight of hydrogen 0·1119 times the increase in weight of the moisture-absorption tube.

CHAPTER VII

DETERMINATION OF NITROGEN

A. DUMAS METHOD

THE Dumas method of determining the nitrogen content of organic compounds consists of burning the material to be analysed in an atmosphere of carbon dioxide. Copper oxide is used as oxidant for the material. Any oxides of nitrogen resulting from the combustion are reduced to nitrogen by means of copper. The liberated nitrogen is collected and measured in a nitrometer, which contains caustic potash solution to absorb the carbon dioxide in the gas.

Certain compounds leave nitrogenous chars, whose final destruction is difficult, when they are burnt in this way. They may, however, be completely burnt in a stream of oxygen after the first combustion in carbon dioxide. We append a description of this modification of the Dumas method.

Attention may be drawn to Gull's method (22) of measuring the nitrogen indirectly in the following way. The gas is collected in a eudiometer over caustic potash solution and, at the end of the combustion, it is forced into a small weighed flask filled with water. The weight of the water displaced by the gas is obtained by re-weighing the flask and the volume of the gas equivalent to the displaced water is calculated. This method is more accurate, in depending on weighings, than the method of measuring the volume of the gas directly and removes the empirical correction applied to the measured volume of the gas for such disturbing factors as the potash undrained from the walls of the nitrometer.

APPARATUS

Carbon dioxide is supplied from a Kipp generator, A (Fig. 15). Its rate of flow is controlled by means of a precision screw-clamp, B. It passes through a small tube, C, with an outlet capillary, this tube being filled with glass wool to retain any drops of liquid which may be carried over from the gas generator. The capillary end of this filter carries the rubber stopper which closes the inlet end of the combustion tube, D. The combustion tube has two fillings: a permanent filling of copper oxide and copper which fills about one-third of the tube from the end nearer the nitrometer, and a temporary filling, consisting of a mixture of the test material and copper oxide. The permanent filling is used repeatedly and should last about 50 combustions. The tem-

porary filling is necessarily renewed at each combustion. The permanent filling is heated throughout its length during a combustion by means of a long burner, E. The temporary filling is heated by means of a bunsen flame, F. The gases resulting from the combustion are

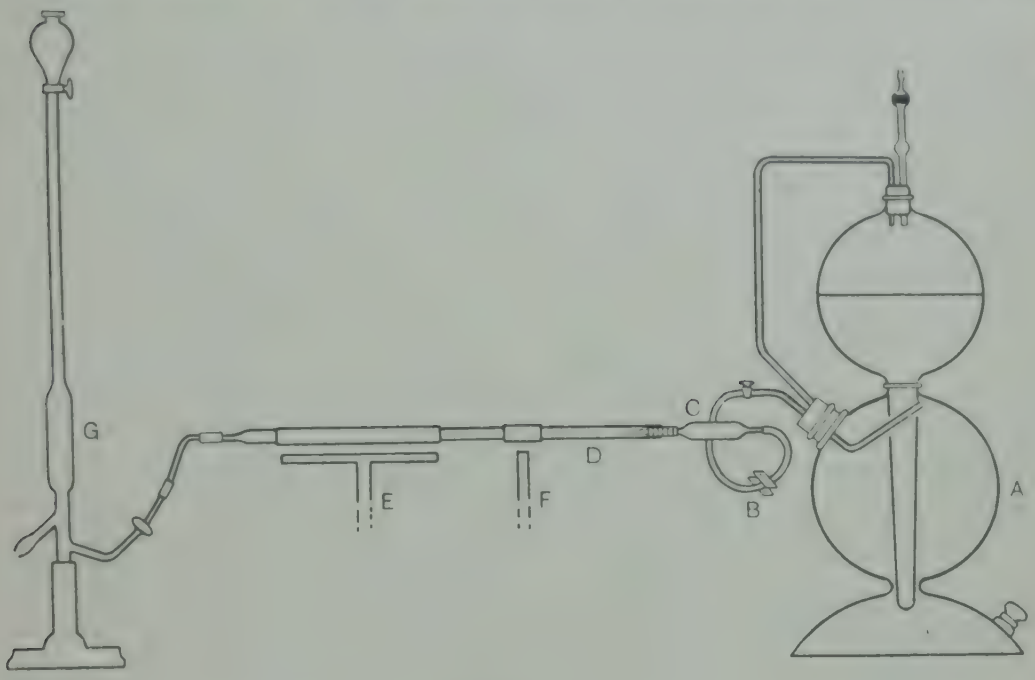

FIG. 15.

collected in the nitrometer G over a solution of concentrated caustic potash solution.

Kipp generator.—The Kipp gas generator has a generating chamber with a capacity of 1 to 2 litres. An ordinary Kipp generator may be used, but it is of advantage to use the Hein modification of it shown in the figure. In this modification the upper acid chamber is closed by means of a rubber stopper carrying a sintered glass funnel, the plate of which is covered with a pool of mercury, and is connected to the middle generating chamber by means of glass tubing provided with a tap. While excess carbon dioxide can escape through the mercury seal in the glass funnel, the seal prevents air leaking into the acid chamber. Air which leaks in is absorbed by the acid and eventually finds its way into the gas chamber, causing appreciable errors in the determination when the carbon dioxide drives it into the combustion tube. As the figure shows, the outlet for the gas from the generator is bent so that the gas is abstracted from the top of the gas chamber.

The generator is prepared as follows: The glass tube connections should be blown and cut to the right length and shape so that when it is filled with marble it may be immediately assembled to prevent the marble, which has been previously de-aerated, re-absorbing air. The

middle chamber is filled to about three-quarters of its capacity with the prepared marble through the side opening, and this side opening is then closed with the tight-fitting rubber stopper carrying the outlet tube with its glass tap and the tube connecting the gas chamber with the upper acid chamber. This rubber stopper should be wired in place. Then sufficient dilute hydrochloric acid to fill the lower acid chamber and about half the upper acid chamber is poured in, and the rubber stopper, closing this chamber and holding the connecting tube and sintered glass funnel, is put in place. The glass funnel should have a layer of mercury about 3 mm. deep. The generator is then purged of air by generating carbon dioxide several times in it by opening the tap in the connection between gas chamber and upper acid chamber so as to bring the acid in contact with the marble.

All the rubber stoppers and connections and the ground-glass joint on the Kipp should be air-tight and it is advisable to ensure their air-tightness by running in Faraday cement at the points where the rubber stoppers meet their glass orifices and at the upper part of the joint where the gas chamber meets the lower acid chamber.

In generating carbon dioxide, care should be taken to generate only a moderate amount of the gas. If too much is generated, the acid in the lowest bulb recedes below the level of the wide tube of the upper acid chamber. Repeated purging of the generator in this way at intervals during one day should ensure that the carbon dioxide finally liberated is of sufficient purity. The purity of the gas is determined by means of a blank on the apparatus. If the blank is excessive, the process of de-aeration is repeated.

The carbon dioxide should be sufficiently pure to give satisfactory *micro-bubbles* in the nitrometer. These bubbles have certain characteristics. They should require at least 20 seconds to rise from the bottom of the column of the caustic potash solution in the nitrometer to the top; they should be nearly absorbed by the caustic solution in the lower, wider part of the nitrometer, overtake each other in the narrow graduated stem and ascend in a closely-packed column.

The appearance of micro-bubbles is not, however, the only guarantee required to ensure that the Kipp generator is in a satisfactory condition. It may happen that micro-bubbles are obtained before combustion is started, but that extraneous air is later passed through the combustion tube if the hydrochloric acid in the generator has absorbed air which has found its way to the gas chamber. A blank is therefore essential to approve the condition of the apparatus.

Precision screw-clamp.—The Pregl precision screw-clamp is suitable for regulating the flow of carbon dioxide. It is placed on the rubber tubing connecting the Kipp generator with the combustion tube and is supported either on a wooden upright fixed to the baseboard on

which the whole apparatus rests or on a stand which supports both it and the near end of the combustion tube.

Water droplet filter.—This filter consists of ½-inch glass tubing about 2 inches long with an inlet tube of 0·6 cm. diameter and an outlet tube of about 2 mm. diameter. It is filled with glass wool before the outlet tube is finally sealed to the body of the filter.

The capillary outlet of this filter carries the rubber stopper which fits into the combustion tube to connect this tube with the generator.

Combustion tube.—The combustion tube is of Supremax glass or silica. The tube may be of the ordinary type similar to that used in the combustion for carbon and hydrogen or, preferably, of the form recommended by Rutgers (21). The combustion tube is cleaned with chromic-sulphuric acid (p. 32), washed and dried before use in the usual way.

If an ordinary combustion tube is used, the permanent filling is as follows : A wad of ignited asbestos wool is pushed into the tube to lie

FIG. 16.

against the capillary snout and form a plug about 4 mm. long. Sufficient coarse wire-form copper oxide, previously ignited for half an hour at about 700° C., is poured into the tube to form a layer about 15 cm. long. Another wad of ignited asbestos wool is then inserted and pushed against the zone of copper oxide to keep it in place. A roll of copper gauze is fashioned by rolling copper gauze with a side of 5 cm. on itself so that it slides into the combustion tube without leaving much space between it and the inner wall of the combustion tube. The roll is so made that its final length is 5 cm. Before inserting it into the tube, it is reduced by heating it red-hot in a bunsen flame and plunging it into alcohol. After this reduction, it is pushed into the combustion tube to lie against the asbestos wad holding the coarse copper oxide in place. Another wad of ignited asbestos wool is inserted into the tube to lie against the reduced copper gauze. This completes the permanent filling.

Rutger's tube (Fig. 16) is a tube 47 to 50 cm. long, 0·8 to 1 cm. in diameter along most of its length with a wider part 12·5 cm. long and 2 cm. in diameter, near the snout end. A length of 5 cm. of the narrower tubing lies between this wider part and the snout. The snout is a capillary tube 2 cm. long and 2 mm. in diameter.

The permanent filling for this tube is as follows : A wad of ignited asbestos is pushed into the tube to lie against the capillary snout and

form a plug about 4 mm. long. A roll of copper gauze, about 4 cm. long, oxidised by heating in the bunsen flame, is pushed into the tube to lie against the asbestos wad and occupy the narrow part of the tube at the snout end. A mixture of coarse and medium copper oxide in the proportions of 1 to 3 is poured into the tube to lie against the copper oxide roll and occupy a length of about 3 cm. of the wide part of the tube. The coarse copper oxide is of the wire form 2 to 3 mm. long and the medium is obtained by grinding this coarse oxide and sieving it upon the 30 (B.S.I.) mesh, retaining that part of the oxide which lies on this mesh for the mixture. Both the coarse and medium copper oxide are heated for about half an hour at 600° to 700° C. before use. This zone of oxide is kept in place by means of a small wad of ignited asbestos. A length of 3·5 cm. from this zone of oxide is filled with the same mixture of coarse and medium copper oxide previously reduced to copper by heating it to a dull red heat in a current of hydrogen or coal gas. A wad of ignited asbestos about 2 mm. long keeps this copper in place. The rest of the wide part of the tube is filled with coarse copper oxide, wire form, kept in place by a short length of copper oxide roll.

The combustion tube, Rutger's or the normal type, is then placed on the combustion stand so that 5 cm. of the tube at the snout end (in the case of the Rutger's tube, the narrower part at the snout end of the tube) overhangs the stand and lies beyond the long burner. This part of the tube containing the copper oxide is thus kept relatively cool during the combustion. The permanent filling in either tube is first heated for about 3 hours in a current of carbon dixoide before making any analyses in it. The tube is then ready for use.

Heating unit.—A long burner is used for heating the permanent filling. It is approximately 16 cm. long and covers both the copper roll and all but the end 5 cm. length of the copper oxide in the permanent filling. This length of copper oxide, as we have observed, remains cold and unheated during the combustion. In order to distribute the heat round the combustion tube and its filling, the long burner directly heats a brass tube, 16 cm. long, which surrounds the combustion tube.

The temporary filling containing the substance to be analysed is heated by means of a movable bunsen-burner which directly heats a brass tube 3 to 4 cm. long round the combustion tube.

Nitrometer.—The nitrometer (Fig. 15) has a narrow graduated stem surmounting a wider tube. The stem is graduated up to 8 ml. in 0·02 ml. It is closed at the top by a large glass tap, above which is a cup to prevent spillage of caustic solution from the nitrometer when gas in the nitrometer is expelled from it. The wider part of the nitrometer has two side arms. One side arm, the upper one, is connected by rubber tubing to a levelling bulb. The other side arm, shaped as

shown, contains a glass tap and is connected to the snout end of the nitrometer by rubber tubing.

Perhaps the most important requirement in the nitrometer is that the graduated stem should widen only gradually to the diameter of the wider bottom part : if the angle of this shoulder is too large, gas bubbles may be caught in it and fail to ascend into the graduated stem.

Before use, and whenever necessary, the nitrometer is cleaned with cleaning mixture (p. 32), rinsed well with tap water, distilled water and acetone in succession and then hung upside down to dry. The taps and rubber tubings are removed and cleaned separately. Taps are lubricated with vaseline, well but sparingly. If too much grease is used on the upper tap, it gives rise to foaming of the caustic solution in the nitrometer. The rubber tubing connecting the nitrometer with the levelling bulb is washed with the caustic potash solution used to fill the nitrometer, never with water. When clean and dry the nitrometer is filled with mercury up to within 1 mm. of the gas inlet tube connected to the combustion tube through the levelling bulb. The levelling bulb is then filled about half-full with concentrated caustic potash solution and raised so as to fill the nitrometer, the upper tap being opened and the tap on the inlet tube being closed during this operation. When the nitrometer is full, there should still remain a little caustic solution in the levelling bulb.

A calibration chart is usually supplied with the nitrometer for correcting its volume to the true volume appropriate to the graduation marks. Otherwise, the analyst should make a calibration of it with mercury. The calibration should be made with the nitrometer inverted. The stem is filled with pure dry mercury, whose density is known by determination, so that its meniscus is near or preferably at the 8 ml. mark. The mercury is run out at 0·1 ml. at a time, weighed and the corresponding volume calculated from the weight. A graph of the true volume, so determined against the volume given by the graduations, enables the true volume corresponding to each calibration to be interpolated. A chart may be then prepared showing the true volume corresponding to each graduation in the following manner:—

	Capacity in ml.				
ml.	·00	·02	·04	·06	·08
·00	*·000*	*·020*	*·040*	*·061*	*·082*
·10	*·101*	etc.			
·20	*·203*				
·30					
·40					
etc.					

Alternatively, a graph may be prepared in which the errors are graphed against the nominal volume as given by the instrument.

Introduction funnel.—For introducing the temporary filling into the combustion tube a funnel is used. It is about 5 cm. long and 2 cm. in diameter at its upper wider part and drawn out gradually to a conical capillary 6 to 7 cm. long and about 5 mm. diameter at its tip. The sides of the funnel should have a gradual slope so that no particles tend to lodge on them. The long stem prevents particles touching the sides of the combustion tube near its mouth and sticking there.

REAGENTS

Marble.—About 2 kg. of clean marble is required for the Kipp generator. It is broken small enough for the pieces to be dropped into the Kipp through the side tubulure. It is purged of air thus. It is washed with dilute (1 : 20) hydrochloric acid, the solution decanted off and the marble then boiled with water in a heavy-walled flask for about 3 hours. The water is changed when necessary until it remains clear. The flask is attached to a water suction pump and the flask evacuated for about 3 hours. To complete the expulsion of air from the marble and saturate it with water, the process is repeated. The marble should be stored under water until it is placed in the Kipp.

Hydrochloric acid.—The hydrochloric acid used for generating the carbon dioxide consists of equal volumes of concentrated hydrochloric acid and either previously-boiled distilled water or the saturated calcium chloride solution from a Kipp apparatus, the acid of which has been exhausted.

Copper oxide.—The coarse copper oxide is in the form of wire 3 mm. long and 0·5 mm. in diameter. It should be free from pores. To obtain the " medium " size, this coarse copper oxide is ground and sieved by means of a 30-mesh (B.S.I.) sieve. That fraction retained by this sieve is the medium size. The fraction passing this sieve is further sieved by means of the 60- and 120-mesh (B.S.I.) sieves and that part of it lying between these sieves kept as the " fine " size. These coarse, medium and fine samples are stored and treated separately. They may be used again, after a combustion, by re-igniting them separately in nickel dishes at about 800° C. They are preferably stored in large test tubes filled with an atmosphere of carbon dioxide.

Mercury.—Purified mercury is used throughout the apparatus.

Potassium hydroxide solution for nitrometer.—Potassium hydroxide of analytical reagent grade purity is dissolved in an equal weight of water. In order to reduce the tendency of this solution to foam in the nitrometer, 2·5 g. of finely-powdered barium hydroxide is added to the

solution for every 100 g. of potassium hydroxide present. After shaking the mixture, it is allowed to stand for half an hour to allow most of the suspended barium hydroxide to settle. The solution is then filtered through a mat of purified asbestos on a Büchner funnel and stored in a bottle with a rubber stopper.

Tap grease.—Heavy vaseline with a lanoline base should be used as lubricant for all taps on the apparatus.

METHOD

Solids.—About 20 mg. of the finely-powdered solid are weighed in a weighing tube and transferred to a mixing tube about 5 cm. long and 1·2 cm. in diameter, provided with a ground-glass stopper. The weight of substance taken is determined from the difference in weight of the charging tube after the substance has been transferred from it.

Heavy liquids and semi-solids.—These are weighed in a porcelain boat and the substance in the boat covered with fine copper oxide.

Liquids.—Liquids are weighed in a sealed capillary (p. 27).

Introduction of temporary filling and substance.—Whether a Rutger's or an ordinary combustion tube is used the introduction of the temporary filling is the same. The combustion tube is detached from the apparatus by first pulling out the rubber stopper from its mouth and disconnecting the snout end from the nitrometer. The rubber tube remains on the inlet tube of the nitrometer. The temporary filling from the previous determination is removed by tapping to a wide-mouthed bottle. The interior of the combustion tube is wiped twice with cotton wool wound tightly round the roughened end of a stiff iron wire about 40 cm. long. A 5 cm. layer of coarse copper oxide is introduced directly into the combustion tube through the introduction funnel to lie against the end of the permanent filling and then a 2 cm. layer of fine copper oxide.

If the test sample is a solid, powdered copper oxide is poured over it to a depth of 2 cm. in the mixing tube, the tube tapped to remove particles of copper oxide from its mouth and the stopper inserted. It is then well shaken to mix the test substance thoroughly with the copper oxide in the tube. After mixing, the tube is tapped, the stopper loosened, the tube tapped again so that no particles will be lost on the stopper, the stopper removed and the mixture poured into the combustion tube through the introduction funnel to lie against the copper oxide already introduced. Another 2 cm. layer of fine copper oxide is put into the mixing tube, the tube shaken, the stopper loosened and the tube tapped and this " wash " material poured into the combustion tube. This process is repeated with another 2 cm. layer of fine copper oxide in the mixing tube. Each time the material is poured

into the combustion tube, the tube is repeatedly tapped to ensure that all particles remaining on the upper part of the tube find their way down to the zone of copper oxide.

If the material is a heavy liquid or semi-solid, which is weighed in a porcelain boat, a 5 cm. layer of coarse copper oxide is first put into the combustion tube, then a 2 cm. layer of fine copper oxide and then the boat pushed in to lie against the copper oxide. Finally, sufficient fine copper oxide is added to cover the boat.

If the substance is a liquid, which is weighed in a capillary, 5 cm. of coarse copper oxide and then 2 cm. of fine copper oxide are put into the combustion tube, the capillary is centrifuged to force the liquid away from the delivery tip, the tip broken off and both the capillary and its tip dropped into the combustion tube, with the open end of the capillary down towards permanent filling. More fine copper oxide is then added to the combustion tube to cover the capillary.

When the sample has been thus introduced, a little coarse copper oxide is added to the filling to form a 3 to 4-cm. layer in the tube. The combustion tube is tapped on the bench while in the vertical position to prevent the temporary filling from spreading, the long and short brass tubes slipped over it from the snout end, the short tube being slipped towards the open end of the tube, the long brass tube being placed over that part of the combustion tube filled with the permanent filling and the tube replaced on the combustion stand. The mouth of the combustion tube and the capillary end are cleaned with cotton wool wound round a knurled iron wire. The capillary end, the rubber stopper and the capillary of the glass inlet tube of the nitrometer are moistened with a trace of glycerine ; the rubber stopper is moistened very sparingly because, if excessively greased, it may be forced out of the combustion tube when it is placed under pressure. The rubber stopper carrying the filter is inserted at the inlet end of the combustion tube and the tube so adjusted that it rests evenly on the combustion stand with the last 5 cm. of the permanent filling protruding beyond the long burner. The snout end of the combustion tube is left disconnected from the nitrometer for the time being.

Preparation for combustion.—The tap on the top of the nitrometer is sparingly lubricated with a trace of vaseline ; the barrel of the tap should become transparent but no grease should enter the stem of the nitrometer ; deposits of grease at this point will cause the potash solution to froth and will lead to high results. The nitrometer is filled with the caustic potash solution by opening the upper tap of the nitrometer, the tap on the side inlet tube being closed, raising the levelling bulb until the liquid enters the funnel on top of the nitrometer, closing the tap and placing the levelling bulb on the lower retort ring or on the bench.

The air is first expelled from the combustion tube. The Kipp generator is filled with carbon dioxide by opening the tap in the connection between the gas chamber and upper acid chamber of the Kipp, letting the acid fill part of the gas chamber and so submerge a little of the marble, and then closing this tap. The tap of the Kipp leading to the combustion tube is then opened to allow the gas to sweep through the combustion tube. The gas is allowed to flow at its full rate for about 3 to 5 minutes. The nitrometer is then attached to the snout end of the combustion tube, its tap on the inlet tube remaining closed. The carbon dioxide is allowed to flow through the nitrometer for about a minute by opening the tap on its inlet tube. This tap is then closed. The nitrometer is again filled with potash by raising the levelling bulb of the nitrometer ; the upper tap on the nitrometer is shut when the nitrometer is filled, the levelling bulb is lowered and the tap on the inlet tube opened. The rate of passage of the bubbles of carbon dioxide flowing into the nitrometer is then adjusted by means of the precision tap at the other end of the train following the Kipp, so that no more than one bubble per second passes into the nitrometer. The bubbles should now be micro-bubbles, showing that pure carbon dioxide is passing and the combustion tube and its connections have been purged of air. If the bubbles are too large so that undissolved gas visibly accumulates at the top of the nitrometer, the sweeping out is repeated until micro-bubbles are obtained. When they are obtained, the tap on the inlet tube is closed, the levelling bulb on the nitrometer raised to discharge the gas from the nitrometer, the top of the nitrometer closed and the levelling bulb once more lowered to the bench.

The outlet tap on the Kipp is now closed and the tap on the inlet tube of the nitrometer opened and the long burner lit after putting the gauze tunnel over the tube. The burner is centred under the tube and its flame adjusted so that it surrounds the brass tube on the combustion tube. The flame should be sufficiently intense to heat the wire gauzes to a dark red. The gas current is continued at the rate of not more than 1 bubble per second until the combustion tube has reached its maximum temperature, when the combustion proper is started.

The combustion is done in two stages. The first combustion is started with the short brass tube just beyond the end of the temporary filling with the bunsen-burner below it. The heating is continued at this point by the bunsen until no more bubbles pass into the nitrometer, showing that the temperature of the combustion tube has come to its equilibrium. The inlet tap on the nitrometer is then closed, the gas in it discharged, the levelling bulb again lowered and the inlet tap on the nitrometer opened. The bunsen-burner and its brass tube are now cautiously advanced over the end of the temporary filling and left there a short while. If any bubbles pass into the nitrometer, it is left in that position until no more pass.

The brass tube and bunsen-burner are then advanced a further 1 cm. over the temporary filling, the passage of bubbles into the nitrometer observed and the heating continued until they cease. If at any stage, after advancing the bunsen-burner, the passage of gas bubbles into the nitrometer exceeds 1 bubble per second in the case of the ordinary combustion tube, or 3 bubbles per second in the case of the Rutger combustion tube, the brass tube and bunsen are withdrawn to their previous position until the evolution of the gas has fallen to the specified value, after which the bunsen and brass tube can be pushed back to their position. When the bunsen and brass tube approach that part of the temporary filling in which the test material is known to be concentrated, they are advanced about $\frac{1}{2}$ cm. at a time and the analyst should be alert to withdraw the bunsen if there is a tendency for the gas flow to exceed 1 bubble or 3 bubbles per second (depending on the type of combustion tube). The whole of the temporary filling should be heated in this way by the movable bunsen-burner up to the permanent filling. When the bunsen-burner has nearly reached the permanent filling, gas will cease to flow into the nitrometer and the mercury in the nitrometer will recede into the inlet tube of the nitrometer towards the combustion tube. The combustion may then be speeded up until the permanent filling is reached.

The combustion is now repeated in the following way: The precision screw-clamp is closed slightly more and the outlet tap on the Kipp generator is opened. The precision screw-clamp is then cautiously opened until not more than 1 bubble per second of gas (3 bubbles with the Rutger's tube) is flowing into the nitrometer. This rate should not be exceeded more than momentarily when manipulating the screw-clamp. This is essential. It may be of some help to watch the speed with which the mercury in the inlet tube of the nitrometer is forced back into the nitrometer by the pressure of the carbon dioxide. The manipulation of the clamp to adjust the speed needs some practice. It is better to have a slow speed of the gas flow than a fast. If the flow is too fast, the nitrogenous gases do not have a sufficient time of contact with the permanent filling. The results may be either too high or too low because of this incomplete contact. On the one hand, there may be dissociation of the carbon dioxide to monoxide and oxygen which are not absorbed in the potash in the nitrometer; on the other hand, there may be incomplete combustion of the material or insufficient contact of the gases with the filling so that the nitrogenous gases are not completely reduced to nitrogen, the nitrogen oxides being absorbed by the caustic potash.

With the gas flow correctly adjusted, the bunsen-burner and its brass tube are now taken to the beginning of the temporary filling and this part of the tube heated for $2\frac{1}{2}$ minutes. The tube and bunsen are then moved forward to the next part of the temporary filling which the brass

tube can cover and this part also heated 2½ minutes. Proceeding in this way, the whole of the temporary filling is re-traversed, each part being heated for the stated period. The bunsen is then extinguished and the flow of carbon dioxide allowed to continue to sweep out residual nitrogen in the tube. Sweeping out is continued until what are essentially micro-bubbles appear. These bubbles are usually slightly larger than the micro-bubbles obtained during the preparation of the combustion tube before the combustion, but should make no appreciable difference to the level of the potash in the nitrometer. When micro-bubbles appear, the long burner is extinguished, the tap on the inlet tube of the nitrometer closed and the nitrometer detached from the combustion tube. The combustion tube is closed at the snout end by means of a rubber cap and allowed to cool in an atmosphere of carbon dioxide from the Kipp until the next combustion is to be made in it; the outlet tap of the Kipp remains open. The levelling bulb of the nitrometer is put in its upper clamp. A thermometer is suspended against the stem of the nitrometer and the nitrometer put in a cool place away from the combustion apparatus.

Gas bubbles trapped in the meniscus of the caustic solution may be detached by lowering the levelling bulb to the bench and striking the rubber connecting tube smartly with the edge of the hand. The levelling bulb is again placed in its upper clamp. After 10 minutes, to allow the caustic solution to drain down the nitrometer, the volume of nitrogen is read by means of a magnifying lens. The temperature of the thermometer and the barometer reading are taken.

The volume of nitrogen so read requires correction, not only to normal temperature and pressure, but also for certain other errors, one of which, the air and absorption error, have to be determined by a blank test. The other errors are due to calibration errors (the determination of which have been described under *Apparatus*) and a miscellaneous set of errors which may be taken as 1·2 per cent. of the total volume of nitrogen collected. These latter include errors due to adhesion of the caustic solution to the nitrometer wall, to the vapour pressure of the solution and an average correction for the reduction of the barometer reading to 0° C. It is unnecessary to determine this class of errors individually, but simply take the empirical correction of 1·2 per cent. of the total volume of nitrogen.

Blank test for determining air and absorption errors. The carbon dioxide supplied by the Kipp generator is never completely free from air, while the copper oxide in the temporary filling always contains some residual air; the error caused by the presence of such air has to be determined by a blank analysis, with a non-nitrogenous substance such as pure sugar being burnt in the combustion tube. About 20 mg. of the sugar is taken and the analysis made on it in the way described

above for nitrogenous compounds. As insufficient nitrogen will be collected during the blank test to reach the first graduation in the nitrometer, some air is allowed to enter the nitrometer to reach the graduations before the combustion proper is begun. The nitrometer containing this air is allowed to come to temperature equilibrium by keeping it for 10 minutes in a cool part of the room, its temperature and the barometric pressure are taken and then the volume of the air in the nitrometer read. The air in the combustion tube is driven out of it and the nitrometer connected with the combustion apparatus. For testing for micro-bubbles, only the minimum amount of carbon dioxide is used. The combustion is then made in the normal manner and the difference between the final volume and the initial volume of gas in the nitrometer, both corrected to normal temperature and pressure, calculated. This difference represents the sum of the air and absorption errors from the carbon dioxide. This error should be constant and vary by not more than $\pm 0{\cdot}005$ ml. over long periods of time. Once its constancy has been established, it is unnecessary to determine it further.

Calculation of nitrogen content.—The nitrometer reading is first corrected for the calibration error of the instrument and from this 1·2 per cent. of the total volume deducted for the miscellaneous errors mentioned above. This volume is now corrected to normal temperature and pressure. From this is subtracted the air-absorption error at normal temperature and pressure. The weight of 1 ml. of nitrogen at normal temperature and pressure is 1·2505 mg. Hence, multiplication by this factor of the corrected volume of nitrogen divided by the weight of substance taken gives the fraction of nitrogen in the material and 100 times this gives the percentage of nitrogen.

MODIFICATION FOR ANALYSING COMPOUNDS DIFFICULT TO BURN

Certain compounds are burnt with difficulty in the Dumas method; on carbonisation they yield a nitrogenous char which cannot be completely burnt after the copper oxide in contact with the material in the tube has been exhausted of oxygen. The difficulty can be overcome by providing a secondary source of oxygen—potassium chlorate is a suitable source—within the tube. The conventional filling of the tube is supplemented by a boat of potassium chlorate. This remains unheated during the first phase of the combustion which follows the course described above. When all the nitrogen from this first phase has been driven from the tube into the nitrometer, the potassium chlorate is heated in order to decompose it; the residual nitrogenous char is burnt at about 600° C. in the atmosphere of oxygen thus pro-

vided. The copper near the unburnt particles is alternately oxidised and reduced until combustion is complete.

The Spies and Harris modification (24) of the conventional Dumas method which applies this principle is described below.

Apparatus.—The only changes necessary in the apparatus described above are a glass tap between the combustion tube and the nitrometer and the provision of a burner, in addition to the other heaters, to decompose the potassium chlorate.

This tap is of the type commonly used on the Pregl nitrometer. The handle of the key of the tap is lengthened to enable the amount of opening of the tap to be accurately controlled. This control is also assisted by scoring the key of the tap with a shallow slot which extends partly round the key from one end of the hole in it. One arm of the tap is bent so that, when the tap is in place, it is parallel to the length of the combustion tube and the other arm is parallel to the gas inlet side arm of the nitrometer. The tap is connected with short pieces of matured rubber tubing to the snout of the combustion tube and the side arm of the nitrometer; both these connections should be glass-to-glass. A precision screw-clamp can be used for regulating the flow of carbon dioxide on the inlet side of the combustion tube, as on the apparatus described above.

The burner for decomposing the potassium chlorate is of the ordinary bunsen type.

Permanent filling of the combustion tube.—The permanent filling of the combustion tube is of the type described above, namely, a wad of asbestos wool at the snout end, then a layer of 15 cm. of coarse copper oxide kept in place by asbestos wool, and then a 5 cm. roll of copper gauze, with another asbestos wad at its outer end to separate the permanent filling from the temporary. The temporary filling is described below.

Weighing and preparation of the sample.—The sample is weighed, with the usual accuracy, in a porcelain boat. The boat, 3 cm. long, is first boiled in dilute nitric acid, drained and then ignited in a bunsen flame. It is allowed to cool in the hand desiccator for half an hour and is then weighed by the method of swings. About 20 mg. of sample (or correspondingly more if the nitrogen content of the material is small) is placed in the boat and spread in a thin layer along the length of the boat. The boat is re-weighed and the weight of sample obtained by difference. The boat is then half filled with fine copper oxide (passing the 60-mesh (B.S.I.) sieve) and the sample and the copper oxide mixed by carefully stirring them with an inch length of 30 S.W.G. platinum wire, flattened at the stirring end. When mixing is complete, the wire is laid on the oxide and the boat filled completely with fine copper oxide. The boat is then kept in the desiccator until it is used.

Temporary filling of combustion tube.—A roll of copper gauze, 1 to 1·5 cm. long and of such a diameter that it fits snugly in the combustion tube, is reduced by heating it in a bunsen flame and plunging it into methyl alcohol. It is slid into the combustion tube to lie against the wad of asbestos wool holding the permanent filling in place. On this is poured coarse copper oxide to form a layer 10 to 11 cm. and on this medium copper oxide is poured to form a layer 0·5 cm. thick. The combustion tube is gently tapped on the bench to settle the temporary filling and then brought to the horizontal. The boat containing the mixture of copper oxide and sample is placed in its mouth, and pushed up the tube with a clean glass rod until it touches the copper oxide. In pushing the boat, it should be kept upright so that none of the material in it is split along the length of the combustion tube. The combustion tube is again tilted and sufficient medium copper oxide poured into it to cover the boat and provide a layer 5·5 cm. long. The tube should not be tilted at too steep an angle during this filling; otherwise, the material may escape from the boat. Finally, a 2 cm. layer of coarse copper oxide is poured upon the medium oxide surrounding the boat.

About 100 to 125 mg. of powdered potassium chlorate is distributed along the length of a 3-cm. porcelain boat (previously ignited and cooled). This boat is pushed into the combustion tube so that it lies about 4 cm. from the coarse copper oxide which completes the temporary filling.

The combustion tube is replaced on its stand, taking care that 5 cm. of the snout end overhangs the long burner. The connections are made at the snout end to the glass tap, which in turn is connected to the nitrometer, and at the other, to the rubber stopper on the regulating glass tap (if this is used), or, if the precision screw-clamp is used, the rubber stopper holding the glass capillary tube, which is connected to the Kipp generator, is inserted into the inlet end of the tube. The heating of the combustion tube, the flushing out, the combustion and the final flushing of the tube are then carried out as described above. Throughout this first phase of the combustion, the boat of potassium chlorate, of course, remains unheated. The gas flow through the tube is regulated by means of the precision screw-clamp or the glass tap at the inlet end of the combustion tube, the tap at the nitrometer remaining opened.

When micro-bubbles begin to form during the flushing of the tube after the first combustion, the regulating tap on the inlet side of the apparatus or the tap on the Kipp generator is closed and the combustion burner for the sample gradually put into place beneath that part of the tube containing the boat which originally contained the sample. The burner for decomposing the chlorate, its flame adjusted to a low height, is gradually put into place at a point about midway be-

tween the boat of potassium chlorate and the mouth of the combustion tube. As the tap on the nitrometer remains open during this heating, the heating by the two burners should be gradual, so that there is no undue increase in the rate of flow of gas into the nitrometer. The burner for decomposing the chlorate is gradually advanced, a few millimetres at a time, towards the boat; its progress should be so slow that the rate of gas flow never exceeds the rate of 2 bubbles per 3 seconds; 15 to 30 minutes are required to advance the burner to the boat and complete the decomposition of the potassium chlorate. When all the chlorate is decomposed the mercury recedes along the side arm from the nitrometer towards the combustion tube as the copper in the combustion tube takes up oxygen. The combustion tube is then swept out in the usual manner and at the usual speed until micro-bubbles appear. The heating by the burner under the sample boat and by the long burner is continued during the sweeping out in order to prevent the copper cooling too much and so failing to absorb oxygen passing through the tube.

The temporary filling is often slightly fused in the combustion, but is easily removed after breaking it up by thrusting a rod into the tube.

When the combustion tube becomes too discoloured to see the filling in it, it may be cleaned, after removing the filling, by washing with water, followed, if necessary, by *aqua regia*.

B. KJELDAHL METHOD

In the Kjeldahl method for determining the nitrogen in organic nitrogenous materials, the material is decomposed by means of sulphuric acid. The decomposition product of the nitrogen, ammonia, is distilled from its solution in the acid after making the solution alkaline, collected in boric acid and estimated by titrating the distillate with standard acid. The digestion of the material with the sulphuric acid is a slow process and several catalysts have been recommended for expediting the decomposition. Of these catalysts, selenium and mercury appear to be the best.

The Kjeldahl method fails for certain materials, such as compounds containing nitrogen linked to oxygen, but its range may be usefully extended to include these by first reducing the material with a mixture of red phosphorus and hydriodic acid and then submitting the reduction product to the Kjeldahl treatment.

The reduction method appears to fail with certain complex materials but for simple compounds containing nitro-, nitroso-, oxime-, hydrazine-, osazone- and azo-groups it works well. If the compound is volatile at the boiling-point of the hydriodic acid, or forms volatile compounds with the acid, it is necessary to reduce it in a sealed tube, but in these circumstances the Dumas method of analysis is to be preferred.

APPARATUS

Digestion flasks.—The flasks used for the digestion are of hard glass or Pyrex and pistol-shaped (Fig. 17), the bulb being of 60 to 70 ml. capacity and the necks 10 cm. long and 1·7 cm. diameter. Alternatively, Pyrex or hard-glass test tubes may be used, 12 cm. long and 2·5 cm. diameter.

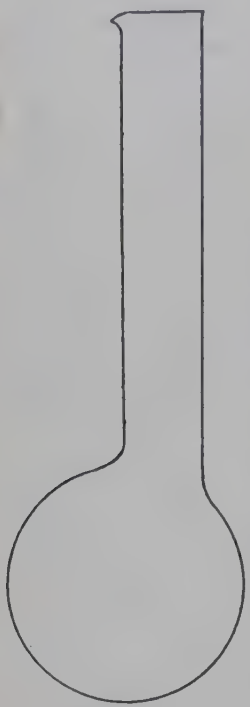

FIG. 17.

Digestion stand.—The Kjeldahl method lends itself to the simultaneous analysis of many compounds. If it is desired to make several analyses at once, the digestion flasks may be supported and heated on a digestion stand. The stand consists essentially of 5 or more micro-burners fed from a common gas tap, a support for the flasks, consisting of an asbestos base plate with holes for the bulbs of the flasks, each hole being above a micro-burner, and a rack to support the necks of the flasks. A combustion stand with separate control for each of the burners is a great advantage.

Distillation apparatus.—The distillation apparatus (Fig. 18) incorporates a device for emptying the distillation flask on completion of a distillation. The apparatus consists of a 1-litre round-bottomed flask, A, for generating steam, the steam trap, B, a 150-ml. distillation flask,

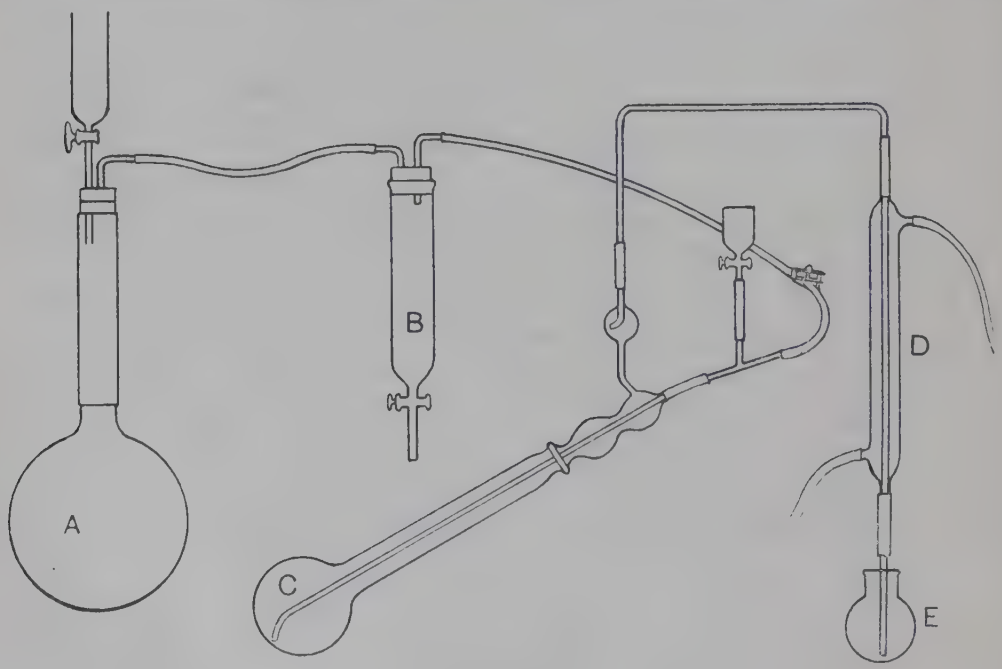

FIG. 18.

C, fitted with a ground-glass joint and carrying the steam-inlet tube and a splash head, a small tap funnel for introducing the solution to be distilled and the alkaline reagent into the distillation flask, a Liebig condenser, D, with a 10-inch jacket, a 100-ml. flask, E, as receiver, and two burners—an ordinary bunsen-burner for generating the steam and a micro-burner for heating the distillation flask during the distillation. The connection to the splash head and the inner tube of the condenser make up a continuous tube of transparent silica, 1 cm. in external diameter and bent twice at right angles. The vertical limb, serving as the inner tube of the condenser, is 32 cm. long, the shorter vertical arm connected to the splash head is 10 cm. long and the horizontal arm 15 cm. long. It is necessary to provide transparent silica connections for this part of the apparatus and for the condenser because the steam dissolves alkali from either Pyrex or ordinary soft glass.

In the diagram the apparatus is shown arranged in a line, but its parts are most conveniently supported by clamps screwed to, and arranged in compact form round, one retort stand.

REAGENTS

Sulphuric acid, concentrated acid, of A.R. standard.

Hydriodic acid, density 1·7.

Red phosphorus.

Sodium hydroxide-sodium sulphide solution.—A 40 per cent. solution of pure sodium hydroxide and a 40 per cent. solution of sodium sulphide are mixed in the proportion of 9 volumes of the first to 1 volume of the second.

Catalyst mixture.—32 gm. of potassium sulphate, 5 gm. of mercury sulphate and 1 gm. of powdered selenium are well mixed by shaking.

Boric acid solution.—A saturated solution of boric acid in distilled water is made by shaking the two together in a bottle. The solution contains approximately 4 per cent. of the boric acid.

Standard hydrochloric acid solution, 0·025 N.—For preparation, see Appendix II.

Mixed methyl red-methylene blue indicator.—0·125 gm. of methyl red and 0·083 gm. of methylene blue are dissolved in 100 ml. of absolute alcohol. If this solution is likely to be kept for longer than a week, it is preferable to make separate solutions and mix as required.

METHOD

Before an analysis, the Kjeldahl digestion flask should be dried in an oven at a temperature above 100° C. About 20 to 50 mg. of the

material to be analysed is weighed accurately on a counterpoised glass scoop and brushed into the dried digestion flask. If the material is to be reduced,* a pinch of red phosphorus on the end of the blade of a penknife is dropped into the flask and 4 ml. of hydriodic acid (density 1·7) are added from a pipette. The acid should be used to wash down any material that may be left on the neck of the flask, though if the flask is dry there is hardly any necessity for this. The flask is put on the digestion stand or supported above a micro-burner, and the height of the burner and of the flask above the burner are adjusted so that the contents of the flask boil gently. The contents are boiled for about 45 minutes (there should be no considerable loss of water during this period) and then to the flask 20 ml. of distilled water are first added, followed by 2 ml. of concentrated sulphuric acid. The solution is now boiled vigorously and the boiling is continued for 45 minutes to expel the iodine from it. The resulting solution is treated as below.

If no reduction is necessary, the material is weighed on the counterpoised glass scoop and brushed into the flask. To it are added 2 gm. of catalyst mixture (conveniently measured from a sample tube with a mark corresponding to the bulk of a 2 gm. sample) followed by 4 ml. of concentrated sulphuric acid. If the compound has been reduced, 2 g. of the catalyst mixture and 2 ml. of concentrated sulphuric acid are added to the solution left after driving off the iodine, as described in the last paragraph. The flask is placed on the digestion stand or over a micro-burner and the contents boiled gently for the first two minutes and then vigorously. The digestion is continued for 45 minutes and then the solution is allowed to cool.†

* Diazo-compounds split off nitrogen when an attempt is made to determine their nitrogen content by the Kjeldahl method. However, they may be successfully analysed by coupling them with phenol so as to form azo-compounds. For this purpose, the test material in the Kjeldahl flask is dissolved in about three times its own weight of phenol by heating the mixture on the water bath. The material is then cooled and the analysis conducted as described in the text with prior reduction of the material.

† It is probably worth interpolating here that it is often and erroneously stated that digestion is complete when the digestion mixture become colourless. There are substances, for example, pyridine carboxylic acids, which do not char with sulphuric acid and the solution becomes colourless immediately the substance dissolves, within the first minute of digestion. During this time, the conversion to ammonia is practically negligible, since these substances are among the most highly resistant to attack in the process. Similarly, compounds that char are not necessarily completely converted to ammonia when the solution clears, but require boiling for some little time after this period. Whether this after-boil is necessary depends on the nature of the compounds. After an investigation of a wide range of compounds, we have found a total time of 45 minutes to be necessary for digestion and this period suffices even for the highly resistant pyridine acids. The digestion may be continued safely for an hour, but after about 90 minutes digestion losses of ammonia occur. We have not yet found a compound which did not yield to a digestion of 45 minutes; a refractory compound which takes longer is probably best analysed by the Dumas method.

In the meantime, the distillation apparatus should have been steamed out if it has been idle for some time. A half-hour's steaming should suffice. During this period, the taps on the steam trap and on the filling funnel for the distillation flask and the screw-clamp on the rubber tubing connecting the steam trap to the distillation apparatus will, of course, have remained opened. After the steaming, the bunsen-burner is removed from the steam generator and the liquid that has collected in the distillation flask is allowed to be drawn back into the trap B as the suction created in the steam generator comes into effect. The trap is emptied of its contents by opening its tap. This tap is left open while the burner is replaced under the steam generator and steam once more generated to blow the liquid out of this trap. The screw-clamp on the rubber connection to the distillation flask is closed. 12 ml. of the alkaline sodium sulphide solution are added to the distillation flask through the tap funnel and any solution remaining on the walls of the funnel is washed into the flask by means of a fine jet of distilled water from a wash bottle. 10 ml. of the saturated boric acid are run into receiver E to a depth of a few mm. so that when the condenser tip is inserted into the flask, its orifice is submerged to a depth of about 1 mm. and remains about 3 mm. from the bottom of the flask.

The digested mixture in the Kjeldahl digestion flask is diluted, when cool, with about 10 ml. of distilled water and transferred to the distillation flask through the tap funnel. The digestion flask is washed three times with distilled water, each washing being transferred to the distillation flask through the funnel. Finally, the funnel is rinsed with distilled water and its tap closed. A little water is left in the funnel to act as a seal. The total volume of liquid in the distillation flask should not exceed half the capacity of the flask; otherwise, priming and frothing may force liquid over into the receiver. The tap on the steam trap is now closed and the screw-clip on the rubber tubing connection opened so that steam passes into the distillation flask. A small (2 cm.) flame of a micro-burner is placed below the distillation flask. When the steam is seen to enter the condenser, the distillation is continued for 5 minutes at the rate of about 4 ml. of distillate per minute. The receiver is then lowered about 5 cm. so that the condenser outlet is about 3 cm. above the level of liquid in the receiver. The distillation is continued about a minute longer with the receiver in this position. Finally, the end of the condenser is rinsed with distilled water with the receiver beneath it to catch the wash water. The contents of the receiver must remain cold during the distillation.

When the distillation is complete, the receiver is removed from beneath the condenser and the burners removed from under the steam generator and distillation flask. As the steam condenses and a partial vacuum is created thereby in the steam generator, the contents of the distillation flask are sucked back into the steam trap, whence they may

be run off. The distillation flask requires no further washing and ready for the next distillation.

The contents of the receiver are titrated with the 0·025 N solutio of hydrochloric acid after adding a few drops of the mixed indicato The titration is taken to the appearance of the violet colour of th indicator. An ordinary 50-ml. burette may be used for the purpose.

Blank test.—It is advisable to run a blank test on the material particularly if the test substance has to be reduced, for the most likel source of extraneous ammonia in the analysis is the hydriodic aci used for the reduction. From this point of view, only the purest aci should be used for the determination. In running the blank, the whol of the procedure described is followed, using sucrose as test material.

The titre obtained from the blank run is subtracted from the titr obtained in the determination. The same blank correction applies t all analyses run with the same samples of reagents, but must b re-determined when a new sample of any of the reagents is used.

Calculation.—As 1 ml. of exactly 0·025 N hydrochloric acid i equivalent to 0·35 mg. of nitrogen, then if V ml. of acid of normality n with respect to 0·025 N is used in titrating the ammonia yielded by w mg. of material, the percentage of nitrogen is the sample is:

$$\text{Per cent. nitrogen} = 35\ Vn/w$$

CHAPTER VIII

DETERMINATION OF SULPHUR

Two combustion methods are described for this determination. In the first, the compound is burnt in a stream of oxygen in a combustion tube, the combustion being completed by passing the gases over hot platinum contacts. The cold part of the combustion tube beyond the heated platinum contacts contains a glass spiral moistened with hydrogen peroxide, in which the combustion gases are absorbed. After washing out the absorbent from the tube at the end of the combustion, the sulphuric acid in it from the sulphur in the compound is determined titrimetrically as follows : Excess standard barium chloride solution is added to the solution from the combustion tube to precipitate the sulphuric acid ; the excess of barium is precipitated by means of potassium dichromate and, after dissolving the barium chromate, it is estimated by titration with a standard solution of ferrous ammonium sulphate.

In the second method, the material is burnt in a rapid stream of air in a silica tube, which is provided with sintered silica discs. The combustion gases are forced through these discs and burn chiefly on their surfaces. The gases are absorbed in hydrogen peroxide and the sulphuric acid in the peroxide from the sulphur in the compound burnt is estimated by titration as above.

Mention may be made of Brewster and Rieman's simplification of the method (23). In general, the solution containing the products of combustion will contain sulphuric acid and such relatively volatile acids as halogen acid, nitric acid and carbonic acid from the other elements present in the analysed compound. Brewster and Rieman found that, by heating the solution under appropriate conditions, all the common acids, which may be present, can be driven off, leaving the sulphuric acid behind. This acid can then be estimated very simply by titration with alkali. The original paper should be consulted for details.

A. CATALYTIC COMBUSTION METHOD

APPARATUS

The apparatus is shown in Fig. 19. A stream of oxygen from a gasholder or a cylinder of the compressed gas is regulated by means of a precision screw-clamp and its speed is measured by a flowmeter, through which it is passed. The stream of oxygen is fed to a combustion tube, A, containing a boat, B, holding the test material. A

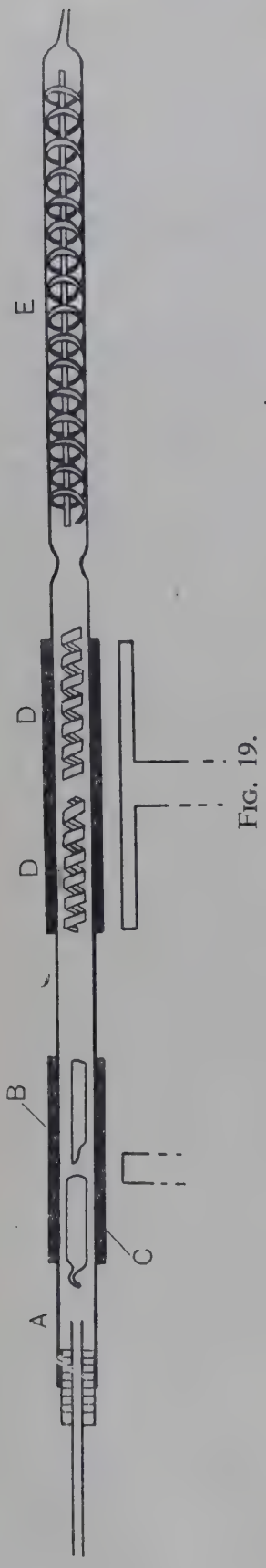

FIG. 19.

hard-glass baffle, C, behind the boat, hinders back-diffusion of the combustion products. The test material is gradually vaporised into the stream of oxygen and is carried to the heated platinum contacts D, D. After leaving these contacts, the products of combustion are carried into a glass spiral, E, which occupies the end part of the combustion tube, where they are absorbed in hydrogen peroxide.

Oxygen supply.—A cylinder of compressed oxygen, which should be fitted with a reducing valve to enable the gas flow to be easily controlled, or a gasholder containing the gas, may be used as oxygen supply.

Precision screw-clamp.—The oxygen supply is connected by rubber tubing to the combustion tube. This tubing has a precision screw-clamp of the Pregl type on it to enable the flow of gas to be accurately regulated. The screw-clamp is conveniently nailed or screwed to the baseboard on which the combustion stand, supporting the combustion tube, is placed.

Flowmeter.—The White-Wright flowmeter, described in the chapter on the determination of carbon and hydrogen (p. 49) may be used for the purpose of maintaining control over the gas flow through the system.

Combustion tube.—The combustion tube is made of Supremax glass and is about 60 cm. long and 1 cm. internal diameter. One end of the tube is drawn out to a capillary of about 0·5 cm. internal diameter and about 3 mm. external diameter. This snout is usually conical in shape. A glass spiral, about 20 cm. long, has one end abutting on this capillary and is kept in place by means of an indentation in the tube near its other end. The mouth of the tube is closed by a rubber stopper carrying a capillary tube.

Combustion stand.—The combustion tube is supported on a combustion stand of the usual type.

Platinum contacts.—The two platinum contacts for the catalytic combustion of the gases are preferably of star shape in cross section. They are 7 cm. long and slightly less than 1 cm. in diameter, so that they fit fairly snugly in the combustion tube. One end of each of the contacts carries a platinum wire hook, which facilitates their removal from the tube by means of a hooked glass rod.

When new, the contacts are cleaned by boiling them in dilute nitric acid and then igniting them in a non-luminous bunsen flame. Before a series of determinations and after about 20 combustions have been made in the tube, they are etched by first boiling them for about half a minute in dilute nitric acid (a 50 per cent. solution in water), dipping them in distilled water, boiling them for about half a minute in dilute hydrochloric acid (a 50 per cent. solution in water) and finally igniting them in the bunsen flame. (The platinum should not come into contact with the inner cone of the flame.)

Glass baffle.—In order to prevent any tendency of the combustion gases to flow against the stream of oxygen, a baffle of hard glass is placed behind the boat containing the test sample. This baffle is 3 to 4 cm. long, closed at both ends and of such a diameter that it slides easily into the combustion tube. It is placed within 1 cm. of the boat of test material. A hook on the end of the baffle facilitates its removal from the tube.

Heating arrangements.—That part of the tube containing the platinum contacts is heated by means of a long burner, the tube being surrounded along this part by means of a brass tube 16 cm. long to distribute the heat round its periphery. This heating tube is placed so that its end is within 5 cm. of the indentation on the combustion tube which holds the glass spiral in place. A wire gauze tunnel is placed above the same part of the tube, being supported in the channels of the combustion stand.

The material is burnt by means of a bunsen flame which heats a short brass tube, 4 cm. long, encircling the combustion tube.

REAGENTS

Dilute hydrogen peroxide.—A solution containing 5 per cent. of Perhydrol or M.A.R. grade in distilled water is used for the absorption of the gases. It should be neutralised before use.

Dilute hydrochloric acid, 2 N.

Dilute ammonia solution (*free from carbonate*), 6 N.—The ammonia is freed from carbonate by adding a solution of calcium chloride to it and filtering off the precipitated carbonate.

Barium chloride, standard solution, 0·025 N.

Ferrous ammonium sulphate, standard solution, 0·025 N.

Sodium hydroxide, standard solution, 0·025 N.

For the preparation and standardisation of these standard solutions see Appendix II (p. 162).

Potassium dichromate, saturated solution.

Barium diphenylamine sulphonate indicator.—A 0·1 per cent. aqueous solution of the solid indicator.

METHOD

Weighing.—Solids and semi-solids are weighed in a platinum boat. Liquids are weighed in a capillary which is placed in a platinum boat for the combustion.

Combustion.—The combustion tube is cleaned by means of cleaning solution (p. 32), tap water, distilled water and acetone in succession. It is dried by aspirating air through it while gently heating it; the air should be filtered through a dust filter (p. 33). One ml. of dilute hydrogen peroxide is poured into a test tube and sucked up to about 1 cm. above the spiral of the combustion tube. After the spiral has been well moistened with the liquid by rotating the tube, the excess is drained off into the test tube and discarded. The combustion tube is placed on its stand and the capillary end covered with the test tube used above. The pre-ignited platinum contacts are inserted in their place in the tube; the first to be inserted is placed so that its end is about 5 cm. from the near end of the spiral and the second is placed about 2 to 3 cm. from the first contact. The brass tube for the long burner is placed over the tube, so that it covers the part of the tube containing the platinum contacts and its end is about 5 cm. from the near end of the spiral in the combustion tube. The brass tube for the combustion burner is also slipped over the tube to lie near the mouth of the tube. The rubber stopper connecting the tube to the oxygen supply is inserted and the oxygen supply adjusted to a rate of 5 ml. per minute. Then the long burner is lit and the platinum contacts heated to a dull red heat.

When conditions are in equilibrium, the combustion tube is opened and the boat containing the test sample is inserted, so that it is within 2 to 3 cm. from the near end of the long burner, followed by the glass baffle placed within 1 cm. of the boat. The combustion is done in the usual way by means of a bunsen flame heating the short brass tube round the combustion tube, and heating is begun with the tube and bunsen about 5 cm. from the platinum boat. The bunsen is gradually

moved towards the boat, about 0·5 to 1 cm. at a time, until the test material shows signs of decomposing, melting or volatilising. The burner is then left in this position for about 10 minutes : if the combustion is conducted too rapidly, unburnt material may be deposited from the gas stream upon the spiral. After 10 minutes, the bunsen is again moved forward cautiously until it reaches the long burner. It is advisable to leave the bunsen for about 5 minutes beneath the platinum boat and allow most of the material, which has passed forward towards the long burner, to be volatilised while the burner is in this position. Combustion will take about 1 hour. After the combustion is completed, both long burner and bunsen-burner are extinguished and the combustion tube allowed to cool in the stream of oxygen. Then the brass tubes are removed from the tube and the platinum boat and platinum contacts are withdrawn from the tube.

Estimation of sulphuric acid in absorbent.—The combustion tube is removed from the combustion stand and its upper part, which was heated during the combustion, wiped with a clean towel. It is then held in an inclined position and 3 ml. of water are sprayed into its mouth, while the tube is rotated to ensure effective rinsing of its inner surface. To avoid loss of absorption liquid during rinsing, the capillary end of the combustion tube is held over the 100 ml. beaker in which the titration is to be made. After rinsing with several portions of distilled water, taking about 7 ml. of water each time and a total of about 30 ml., the collected washings in the beaker are gently boiled for 2 minutes with a rough platinum wire inserted into the solution to destroy the peroxide. After cooling, the solution is neutralised with 0·025 N sodium hydroxide solution. The volume of caustic solution necessary for this purpose gives the minimum amount of standard barium chloride solution which must be added for the precipitation. Sufficient 2 N hydrochloric acid solution is added to the solution to make it approximately 0·1 N with respect to this acid. The solution is then heated to boiling and 0·025 N barium chloride solution added drop by drop until an excess of about 5 ml. has been added ; the volume of barium chloride solution is, of course, accurately measured either from an ordinary macro-burette or from a pipette of suitable capacity. The solution is digested for 4 minutes, made slightly alkaline by adding 6 N ammonia (free from carbonate) and 10 ml. of saturated potassium dichromate solution added slowly. The solution is cooled, filtered through an Emich porcelain or glass filter-stick and the precipitate washed three times with 5 ml. portions of distilled water. The barium chromate precipitate on the filter-stick is dissolved in warm 2 N hydrochloric acid, the solution cooled, 0·1 ml. of barium diphenylamine sulphonate indicator added and the solution titrated with 0·025 N ferrous ammonium sulphate solution to discharge the blue colour. The weight of sulphur in the precipitated sulphate is :

mg. sulphur = 0·4 (ml. 0·025 N barium chloride added $-\frac{2}{3} \times$ ml. 0·025 N ferrous ammonium sulphate used).

If the substance contains only carbon, hydrogen and oxygen in addition to sulphur, the sulphuric acid may be estimated by titration with alkali. For this purpose the combustion tube is washed out and the hydrogen peroxide in the solution destroyed as above. The solution, when cooled, is titrated with 0·025 N sodium hydroxide (of accurately known normality) using mixed methylene blue-methyl red indicator to detect the end point. The preparation of the mixed indicator is described under *Determination of Nitrogen: Kjeldahl Method* (p. 89).

B. SURFACE COMBUSTION METHOD

In this method, the material is burnt in air in a silica combustion tube, which contains two heated sintered silica discs. The combustion gases have to pass through these discs, and are burnt by surface combustion, thus completing the combustion of the sulphur gases to sulphur trioxide. The gases are absorbed in hydrogen peroxide and the sulphuric acid in the solution is determined titrimetrically by the method given above.

APPARATUS

The apparatus (Fig. 20) consists essentially of two parts, the combustion tube, A, and the absorber, B, containing hydrogen peroxide.

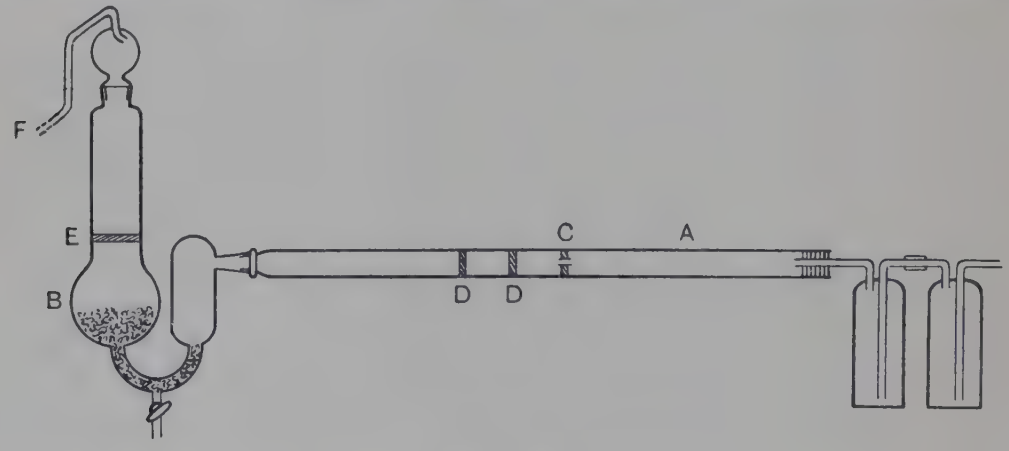

FIG. 20.

The silica tube, A, is 45 cm. long and 1·2 cm. in diameter. Near the middle are two silica filter plates, D, 3·5 cm. apart, and a plate, C, having a central 3-mm. hole in it. That part of the tube holding the filter plates is jacketed with asbestos paper kept in place with asbestos string. This part of the tube is heated strongly by means of a flat-flame burner over a distance of 6 cm.

The outlet end of the combustion tube makes a ground-joint connection with the absorption vessel, B. The tap below the U-bend of this vessel enables the vessel to be emptied. The wide body of the vessel on the left arm of this U-tube has a sintered silica plate E, fused close to its base. The U-tube below this wide part is partially filled with glass beads. Sufficient hydrogen peroxide of 5 per cent. strength is filled into this absorption vessel through its upper tubulure to cover the beads.

The outlet of the absorption vessel is closed by a stopper with a glass tube, F, which is connected to a water pump; this draws the air for the combustion of the material through the apparatus.

A bunsen-burner is used to burn off the material in the boat in the combustion tube.

Two wash bottles containing a 10 per cent. solution of caustic potash are connected to the inlet of the combustion tube for the purpose of washing the air used for the combustion.

REAGENTS

Hydrogen peroxide, 5 per cent.—One volume of hydrogen peroxide (30 per cent. strength) is diluted with 5 volumes of distilled water and neutralised.

Potassium hydroxide solution, 10 per cent.—10 gm. of potassium hydroxide are dissolved to give 100 ml. of solution to serve as wash liquid for the air used in the combustion.

The other reagents are given under the description of the catalytic combustion analysis for sulphur (p. 93).

METHOD

About 20 mg. of the material (or more if the sulphur content is low) are weighed accurately into a porcelain or platinum boat and inserted into the combustion tube to within 1 to 2 cm. from the first silica plate in the tube. The wash bottles at the inlet end of the tube are then attached and heating of the asbestos paper round the sintered silica plates is begun.

Four ml. of the 5 per cent. hydrogen peroxide in a glass tube, having a rubber bulb attached to it, are blown into the U-bend of the absorption vessel through the side arm which connects it to the combustion tube and 4 ml. of the peroxide are added through the top of the vessel, flooding the sintered glass plate in the wide body of the vessel. The opening of the absorption vessel is closed by the rubber stopper and its glass tube connected to the water pump. It is advisable to have a safety trap on this connection to the water pump to prevent the water from the pump flooding the absorption vessel; a small empty absorption bulb serves this purpose.

The absorption vessel is now connected to the combustion tube

through the ground joint. This joint should not be lubricated; the connection is made by pushing the male joint of the combustion tube well home into the joint of the absorption vessel. The flow of air through the apparatus is adjusted so that 4 to 6 bubbles rise per second through the peroxide covering the beads in the absorption vessel.

When the asbestos paper round the sintered silica plates has reached its maximum red heat, the combustion of the material in the boat is begun. Combustion is started at the front end of the boat, the end nearer the inlet, with a small flame on the combustion burner. If the material carbonises, the combustion of the material is relatively simple. If it does not carbonise but distils or decomposes, the combustion should not be made so rapidly that carbon or tar products separate out on the other side of the sintered silica plates. With such materials the combustion should be done relatively slowly.

To burn off the material, the small flame of the bunsen is gradually taken across the boat; in doing so, that part of the combustion tube beyond the sintered silica plates should be constantly watched to see that no decomposition of carbon or tar occurs there. The material may be finally heated with the full flame of the bunsen to complete the combustion. Even with substances that require care in burning off, the combustion should be completed in about 15 minutes.

During the combustion, sulphur trioxide condenses in the exit end of the tube. This must be driven off, starting with the bunsen at the inlet side of the deposit and traversing it in the usual way. The movement of the deposit can be clearly observed. Finally, the ground joint between the combustion tube and absorption vessel is heated to drive off any sulphur trioxide that may have settled there. The heating may be discontinued when there is no longer a mist of sulphur trioxide in the absorption vessel.

The absorption vessel is now emptied through its tap into a 250 ml. beaker and the vessel rinsed out three times with distilled water. The volume of solution finally obtained should be about 50 ml.

Titration of the sulphate in the solution.—The sulphate in the hydrogen peroxide obtained from the combustion is estimated titrimetrically in the same way as in the catalytic combustion (p. 97) using a macro-burette.

If the compound contains both sulphur and chlorine or bromine in addition to the carbon, hydrogen and oxygen, the sulphur and the halogen may be determined in one combustion as follows: The total acidity (sulphuric acid plus halogen acid) of the absorbent, after treatment, is determined by titration with alkali. The halide content of the neutral solution is then determined in the way described in Chapter IX, *Determination of Halogens*, by titrating with a standard solution of silver nitrate, using an adsorption indicator for detecting the end point. The sulphur is found by difference from the results of the alkali and silver nitrate titrations.

CHAPTER IX

DETERMINATION OF HALOGENS

The substance is burnt in a combustion tube in a stream of oxygen: to ensure complete decomposition, the products of the combustion are passed over platinum contacts. The halogen is absorbed either in heated barium carbonate (chlorine and bromine) or in sodium hydroxide solution (iodine). The absorbent is suspended in water or dissolved, treated appropriately and its content of halide determined by titration.

In the combustion in oxygen and in the presence of a platinum catalyst, chlorine is evolved wholly as HCl; bromine is evolved partly as HBr and partly as free bromine; iodine is evolved wholly as the element.

Barium carbonate, heated to dull red heat, quantitatively absorbs both the chlorine and bromine without the formation of oxy-halogen salts, and both the barium carbonate and the barium halides are non-volatile under these conditions. If chlorine is being determined, the element can be determined at once by suspending the barium carbonate containing the halide in water and titrating with silver nitrate, using dichlorfluorescein as indicator. For this titration, the solution should be neutral—as it is if the suspension is not treated in any way before titration. Bromine can be determined in the same way, but a sharper end point is obtained by using eosin as the indicator and dissolving the barium carbonate in nitric acid. The acidity is reduced to a small value before the titration is made.

The determination of iodine requires a rather more complicated procedure. The products of combustion are absorbed in a solution of sodium hydroxide. During the absorption, sodium iodide and iodate are formed by the liberated iodine. The iodide in the solution is oxidised by means of bromine to iodate. The total iodate so obtained is liberated as iodine by acidifying the solution after adding potassium iodide. The liberated iodine is titrated with sodium thiosulphate solution.

A. DETERMINATION OF CHLORINE AND BROMINE

APPARATUS

Gaseous oxygen is supplied from a cylinder of the compressed gas or from a gasholder. Its speed is regulated by a precision screw-clamp on the rubber tubing connecting the cylinder or gasholder with the

combustion tube (Fig. 21). The gas flow may be measured from a flowmeter inserted in the tubing leading to the combustion tube. The oxygen passes at once to the combustion tube A which is of uniform diameter from end to end. Both ends are closed by rubber stoppers. The stopper at the inlet end carries the glass tube connected to the flowmeter or oxygen supply. The rubber stopper at the outlet end carries a bubbler, B, containing silver nitrate solution, which serves the double purpose of showing the rate of gas flow and of detecting any halogen-laden gas which may have escaped absorption in the tube. If it turns cloudy, the analysis has failed ; under correct conditions of manipulation, the solution in it will remain clear.

The material to be analysed, contained in a boat, C, placed towards the inlet end of the combustion tube, is burnt off by the movable burner, D. The boat is preceded by a baffle of resistance glass, E, to prevent the burnt gases reversing in direction. Following the boat are the platinum contacts, F, heated by a long burner, G, for the catalytic

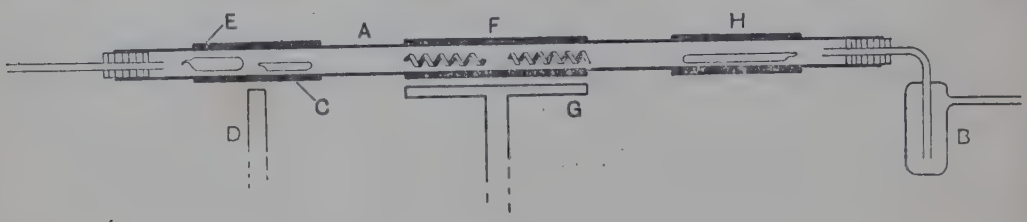

FIG. 21.

oxidation of the gases. This is followed by a boat, H, containing barium carbonate, which is heated by a bunsen-burner and absorbs the halogens from the gases.

Oxygen supply.—A cylinder of compressed oxygen, which should be fitted with a reducing valve to enable the gas flow to be finely adjusted, or a gasholder of the gas, may be used as oxygen supply.

Precision screw-clamp.—The oxygen supply is connected by rubber tubing to the combustion tube. This tubing has a precision pinch screw-clamp of the Pregl type on it to enable the flow of gas to be accurately regulated. This screw-clamp is conveniently nailed or screwed to the baseboard on which the combustion stand supporting the combustion tube is fixed.

Flowmeter.—The White-Wright flowmeter (p. 49), may be used for the purpose of maintaining control over the gas flow through the system. It is not absolutely essential, sufficiently accurate control may be obtained from the rate of bubbling of the gases through the bubbler, B, at the outlet end of the combustion tube. The rate of bubbling may be calibrated, while the bubbler is in place on the apparatus, by means of a calibrated flowmeter.

Combustion tube.—Unlike the combustion tubes used in most of the determinations described in this book, the combustion tube for the halogen determination has no snout at the outlet end but has the same diameter throughout its length. It is approximately 50 cm. long and 1 cm. in internal diameter, with a 1-mm. wall. It should be made of Supremax glass or silica. A new tube is cleaned in the usual way, washed and dried. During the combustion, water tends to condense towards the two ends of the tube. If it does, the tube should be wiped dry by means of cotton wool on the end of an iron wire before the next combustion is attempted.

Glass baffle.—In order to prevent any tendency of the combustion gases to back up and reverse the stream of gas, a baffle of hard glass is placed in front of the boat containing the test sample and within 1 cm. of it. This baffle has been described in the last chapter (*Determination of Sulphur*, p. 94).

Boat for test sample.—The boat for the test sample is preferably a platinum one, though a porcelain boat may be used.

Platinum contacts.—Two platinum contacts are used for the catalytic oxidation of the gases. They are each 5 cm. long and may be star-shaped in cross section or be made from platinum foil, 0·05 mm. thick, wound in the form of a loose roll to fit loosely in the tube. Before use, the contacts are etched by boiling first in a 1 : 1 solution of hydrochloric acid in water, lightly rinsing with distilled water, then boiling in a 1 : 1 solution of nitric acid in water and finally heating red-hot in the flame of a bunsen-burner. The contacts should be re-etched after about 20 combustions.

Boat for barium carbonate.—About 0·5 g. of barium carbonate is used for the absorption and is contained in a porcelain boat approximately 4 cm. long and 0·5 cm. wide. The barium carbonate is spread evenly over the bottom of the boat.

Heating unit.—The platinum contacts are heated throughout the combustion by a long burner about 16 cm. long which directly heats a brass tube surrounding that part of the combustion tube containing the platinum contacts. The boat containing the barium carbonate is heated by means of a bunsen flame which directly heats a brass tube 4 cm. long round that part of the combustion holding the boat of carbonate. The test material is heated by a movable bunsen-burner through the intermediary of a third brass tube 4 cm. long. All the brass tubes fit fairly loosely over the combustion tube.

Combustion stand.—The tube may be supported either on the usual type of combustion stand or by means of retort clamps at the two ends of the combustion tube.

Outlet bubbler.—The outlet end of the combustion tube is close by a rubber stopper carrying a small bubbler. A suitable bubbler the Pregl type. The bubbler contains a little 5 per cent. silver nitrat solution acidified with nitric acid, sufficient to submerge the interna delivery tip of the bubbler by about 2 mm.

REAGENTS

Barium carbonate.—Solid barium carbonate of analytical purity used for the absorption of the halogens in the combustion product It should contain negligible amounts of halide and may be tested thus About 0·5 gm. of the carbonate is dissolved in a 7 per cent. solution o halide-free nitric acid (" M.A.R." grade). To the solution is adde 0·5 to 1 ml. of 5 per cent. silver nitrate solution and the liquid heate for 15 minutes on a water bath. The sample of the carbonate i satisfactory if the solution shows no turbidity.

Standard silver nitrate solution, 0·02 or 0·05 N strength.—Fo preparation, see Appendix. If a micro-burette is used for the titration a 0·05 N solution is prepared ; if a weight burette, a 0·02 N solution which is standardised against potassium chloride.

1. *For chlorine determination.*

Dichlorofluorescein indicator.—0·1 per cent. solution of the indicato in distilled water.

2. *For bromine determination.*

Dilute nitric acid.—A 7 per cent. solution of concentrated acid in water. This solution is made from halogen-free nitric acid, M.A.R. grade.

Sodium hydroxide solution, 25 per cent. strength.—This solution is made from pure sodium hydroxide.

Eosin indicator.—0·5 per cent. solution of the indicator in distilled water. The analyst should make sure that the eosin is of the grade suitable for use as an adsorption indicator. In our experience the samples of eosin available differ appreciably in their suitability.

Phenolphthalein indicator.—A solution of 0·1 per cent. of the indicator in absolute alcohol.

METHOD

Solids.—About 20 mg. of sample (preferably about 30 mg. if bromine is to be determined) are weighed out into a platinum boat which is put into the micro-desiccator.

Heavy liquids and semi-solids.—Like solids, these, being non-volatile, are weighed in a boat.

Liquids.—Liquids are filled into a weighing capillary, containing a little ammonium nitrate instead of the potassium chlorate used for the determination of carbon and hydrogen. The method is described on p. 27. Before being introduced into the combustion tube upon a boat or foil of platinum, the capillary is again centrifuged, its tip broken off and the tip and capillary placed in the boat or foil so that the open end faces downstream towards the heating unit.

Combustion.—The platinum contacts in the tube are spaced about 1 cm. apart, while that contact nearer the outlet end is about 8 cm. from that end. The brass tube for the long burner should cover that part of the tube containing the platinum contacts. The absorption boat is filled with not more than 0·5 gm. of barium carbonate and the carbonate distributed over the bottom of it. This boat is now inserted into the outlet end of the tube so that its inner end is within about 2 cm. of the end of the nearest platinum contact. The rear part of the combustion tube from this end of the contact overlaps the combustion stand. The brass tube for this boat is slipped into position to overlie the boat and the bunsen-burner for heating it is placed centrally, or if anything rather towards that end of it nearer the platinum contact. The rubber stopper carrying the bubbler with silver nitrate is put into place.

The boat containing the test sample is now inserted so that it is about 2 to 3 cm. from the end of the brass tube heated by the longer burner, and the glass baffle inserted so that its end is within about 1 cm. of the boat. The rubber stopper is inserted at the inlet end of the combustion tube and the flow of oxygen adjusted to a rate of 5 ml. per minute by means of the precision screw-clamp. The rate of bubbling through a Pregl bubbler will be about 2 bubbles per second.

The heating gauze is now put above the long burner. The long burner and the bunsen-burner beneath the boat of barium carbonate are both lit and allowed to reach their equilibrium temperature. The long burner flame should be adjusted to surround the brass tube above it and heat it to a dull red. The bunsen flame should be at about full height so as to heat that part of its brass tube on which it impinges to a moderate red heat.

When conditions in the tube and its heating are stable, the bunsen for burning off the sample and its brass tube are moved to within about 5 cm. of the boat. When its brass tube is fully heated, it is gradually moved about 1 cm. or preferably 0·5 cm.

at a time towards the sample boat in the combustion tube, care being taken to observe the behaviour of the sample. As soon as the sample shows signs of responding to the heat, the bunsen is kept still for some moments so that the analyst may decide how the combustion should be effected. The conditions of the combustion described in the determination of carbon and hydrogen (p. 69) should be followed. The speed at which the material is heated will depend on its volatility as disclosed by its behaviour when it begins to respond to the heat. The first stages of heating should be passed relatively slowly and conducted so as to distil the material or its tarry decomposition products about 2 cm. or so in front of the boat. Care should be taken that the vapours do not condense in contact with the boat. An indication of too rapid combustion is the appearance of a fairly dense mist in the tube. This should be avoided ; if it is not avoided, as soon as the mist appears the bunsen should be withdrawn and the combustion tube at the spot cooled by blowing upon it. When the bunsen reaches the boat it is allowed to remain under it for about 5 minutes and is then again moved forward to drive the drop of oil in front of it forward. When this oil drop remains stationary as the bunsen is advanced, the bunsen should be moved only cautiously so that the evaporation of the drop is not too rapid. After its evaporation, the bunsen may be moved rather rapidly over the boat and towards the long burner to burn off any residue that may be left in the tube.

The combustion tube towards the outlet end should be periodically inspected for signs of material that may have distilled and passed unchanged through the tube, and the silver nitrate in the bubbler for signs of decomposition of halide in it, showing incomplete absorption of the halogen vapours in the barium carbonate.

As usual, the heating of the boat section of the combustion tube by the movable burner is repeated, but more rapidly than the first heating. The bunsen and brass tube for the combustion are taken back to their original position and the movement of them over the boat repeated, the repetition taking 5 to 10 minutes.

After combustion, the long burner and the burner beneath the boat of barium carbonate are extinguished and the tube allowed to cool somewhat while the oxygen still flows. The rubber stopper at the outlet end is then taken out and the boat of barium carbonate withdrawn by means of a hooked glass rod. Care should be taken not to spill any of the carbonate in the tube. The boat is put in a 100-ml. beaker and its contents washed into the beaker with the minimum amount of water. If any carbonate has been spilt in the combustion tube, this tube is emptied of its contents and the carbonate in it washed with the minimum of water into the beaker. This washing should, if possible, be avoided by care in withdrawing the boat from the combustion tube. The treatment of the suspension in the beaker of the

barium carbonate differs according as chloride or bromine is being determined.

Determination of chlorine.—After washing the barium carbonate into the beaker, the particles are crushed with a glass rod having a flattened end to bring all the barium chloride into contact with the water. Ten drops of 0·1 per cent. solution of dichlorfluorescein in water are added and the solution titrated with the standard silver nitrate solution. The titration should be done either from a micro-burette or a weighing burette out of any direct sunlight. If the micro-burette is used the titration is made with 0·05 N solution, whereas it is permissible to use a 0·02 N solution with a weighing burette. The solution is continually swirled during the titration and care should be exercised in adding the silver solution when the pink colour in the halide solution begins to persist. Towards the end point, it is advisable to try to split the drops from the burette by touching the drop on the burette tip, which has not been allowed to grow of sufficient size to fall, to the inner wall of the neck of the beaker and washing it down with the minimum of water into the solution. The end point is reached when the pink colour of the solution is permanent. A valuable verification is the coagulation of the silver halide which can be seen forming in threaded clots on the surface of the solution.*

Determination of bromine.—The contents of the boat of barium carbonate from the combustion tube are tipped into a 100-ml. beaker, the boat being rinsed into the beaker by means of a little nitric acid solution of 7 per cent. strength. The beaker is tilted slightly and the barium carbonate dissolved in the minimum amount of this dilute nitric acid. If the concentration of the solution is too strong, barium nitrate is precipitated and this must be re-dissolved by adding a little water. After adding a drop of phenolphthalein solution, a 25 per cent. solution of sodium hydroxide is added in drops until the solution turns red. This addition is best made from a burette. The dilute nitric acid solution is then added dropwise to the solution from another burette with continuous shaking until the solution becomes slightly acid, as shown by the discharge of the colour of the phenolphthalein. About 2 drops more of the acid are added and then a few drops of a 0·5 per cent. eosin solution. The total volume of the solution, which is now ready for titration, should not exceed about 10 ml. The first addition of the silver nitrate during the titration should be made rapidly until the drop of silver solution turns the solution a

* Bobranski and Sucharda (1) recommended that starch should be added to the solution before titration is done to prevent the coagulation of the silver halide. They claim that this addition increases the sharpness of the end point. We have found any such increase to be inappreciable, and the addition of the colloid certainly inhibits the verification of the end point by the formation of the coagulum.

deeper red slightly tinged with violet where it enters the solution.* The titration is then made dropwise until the change of colour permeates the solution and remains when the solution is shaken. The end point is verified by the signs of coagulation of the precipitate that may be seen on the surface of the solution.†

As 1 ml. of 0·02 N silver nitrate is equivalent to 0·71 mg. of chlorine and 1·60 mg. of bromine, the percentage of chlorine in a compound is 71 Vn/w and of bromine 160 Vn/w where V ml. of the silver nitrate is used, of normality n with respect to 0·02 N, to titrate the solution given by a wt. of w mg. of compound.

B. DETERMINATION OF IODINE

The following is a modification of Leipert's method (27) for determining iodine. The material is burnt in a stream of oxygen in a combustion tube containing a spiral glass filling. The combustion gases are absorbed in caustic soda solution dispersed over the spiral filling. Most, if not all, of the iodine is oxidised to iodic acid; any iodine which remains in the state of iodide in the absorption solution is oxidised to iodate by means of bromine. The iodate in the solution is liberated as iodine by the addition of potassium iodide and the iodine determined by titration with sodium thiosulphate.

APPARATUS

The apparatus is the same as that described for the catalytic combustion of materials for the determination of sulphur (p. 93). The combustion tube (Fig. 19) is about 65 cm. long and of 0·8 to 1 cm. diameter and is drawn out at one end to a capillary tube about 0·5 mm.

* The titration of chloride by means of silver ion using dichlorfluorescein as indicator gives an end point which is unmistakable even to the untrained eye. This is not altogether true of the titration of halides using eosin as indicator; the colour change at the end point is from a yellowish-red to a deeper red slightly tinged with violet. The difficulty arises from the fact that both colours are predominantly red. It is useful for the analyst who is unfamiliar with the titration to have some practice with solutions of known strength (about fiftieth normal) of bromide and silver to familiarise himself with the change.

† We may mention that Hölscher has described a semi-micro combustion method for determining chlorine and bromine which is based on the Pregl micro-method and is similar to the combustion method described in this book for the determination of sulphur by combustion in oxygen. The material is burnt in the usual way in a combustion tube, complete combustion being ensured by passing the combustion gases over platinum contacts. The gases are absorbed in hydrogen peroxide distributed over an internal spiral in the combustion tube. After the combustion, the hydrogen with its hydrogen halide is washed out of the tube, the solution boiled, cooled and titrated with silver solution using the appropriate adsorption indicator. The method takes about the same time as the method described above—on the whole being rather slower when chlorine is determined. If, however, the substance does not contain nitrogen or sulphur, the washings may be titrated with N/50 alkali.

inner diameter. A glass spiral about 20 cm. long is held within the tube at the capillary end by means of an indentation in the tube.

The combustion is catalysed by means of two platinum contact stars, each about 5 to 7 cm. long. The star nearer the spiral is placed within about 2 to 3 cm. of the spiral and the other star about 1 cm. from the first. The stars are etched before use in the usual way by means of hydrochloric and nitric acids (p. 95). They are heated throughout the combustion by means of a long burner placed beneath them, the flame of this burner impinging on a brass tube about 16 cm. long surrounding that part of the combustion tube holding the stars.

The combustion tube is supported suitably on a combustion stand. Its open end is provided with a rubber stopper holding either a piece of capillary tubing or, preferably, the outlet tube of a small Pregl bubble counter containing 5 per cent. sodium hydroxide as washing liquid. The bubble counter may serve as a flowmeter, after the rate of bubbling has been calibrated against a known flow of oxygen. The bubble counter or capillary glass tubing is connected to a gasholder of oxygen or a cylinder of the compressed gas. If the capillary only is used as oxygen inlet to the tube, a calibrated flowmeter of the usual type should be inserted in the tubing connecting the capillary to the oxygen supply.

The material to be analysed is contained in a platinum or porcelain boat placed inside the tube within about 4 cm. from the long burner. The material is burnt off by means of a bunsen-burner, the flame of which heats a brass tube, 4 cm. long, round the combustion tube.

REAGENTS

Sodium hydroxide solution.—15 gm. of caustic soda are dissolved in 100 ml. of water.

Aqueous sodium acetate solution.—A 20 per cent. solution of the trihydrate of sodium acetate in water.

Sodium acetate solution in glacial acetic acid.—10 gm. of the trihydrate of sodium acetate are dissolved in 100 ml. of glacial acetic acid.

Bromine (M.A.R. grade).

Formic acid, 80 to 100 per cent. strength.

Potassium iodide.—A 10 per cent. solution; the sample of iodide used for the solution should be free from iodate.

Sodium thiosulphate solution, 0·025 N.—For preparation and standardisation of this solution, see Appendix II.

Sulphuric acid, 2 N.

Starch solution.—Triturate 2 g. of starch (preferably the soluble form) and 1 g. of salicylic acid to a thin paste with a little water and pour the paste into 500 ml. of boiling distilled water. Boil until the solution is clear, cool and transfer to a glass-stoppered bottle.

Methyl-red, 0·1 per cent. solution.—0·1 g. of the indicator is dissolved in 60 ml. of alcohol and the solution made up to 100 ml. with distilled water.

METHOD

The spiral combustion tube is cleaned by immersing it in chromic-sulphuric acid (p. 32) for some hours, draining it and washing it first with tap water, followed by distilled water and finally rinsing with acetone or alcohol. It is dried at the suction pump, preferably with gentle warming. About 5 ml. of the 15 per cent. caustic solution is placed in a test tube of 3 cm. diameter and aspirated into the spiral tube so that its level when it is drawn up does not rise higher than the top of the spiral. The solution is allowed to drain back into the test tube, this excess being rejected. The combustion tube is placed on its stand, the two platinum stars inserted, the two brass tubes slipped over it so that the tube for the long burner surrounds that part of the combustion tube containing the platinum stars, and that for the bunsen-burner is left near the open end of the combustion tube. The rubber stopper with the inlet tube for the oxygen is inserted into the mouth of the combustion tube and the oxygen flow started at 5 ml. per minute. The long burner beneath the platinum stars is lit and the temperature of the tube allowed to come to equilibrium.

The rubber stopper closing the tube is now taken out and the boat containing the test sample is inserted so that it lies within 4 cm. of the long burner. The stopper is replaced and the oxygen flow continued.

Combustion.—The combustion is made in the normal way. The bunsen tube for burning off the sample is placed near the inlet end of the combustion tube at a distance of about 5 cm. from the boat containing the sample, with its brass tube, surrounding the combustion tube, above it. The bunsen-burner is gradually advanced to the sample and the first signs of decomposition or similar behaviour in the sample observed. More caution is needed in this determination than normally, for great care should be taken, particularly in the decomposition of the material, that no iodine separates out behind the movable burner. If any iodine does so separate, it must be driven back, if possible, by slowly heating the tube.

When the combustion is complete, the tube, while still hot, should be examined for any iodine that may have separated out on the cooled

wall of the tube between the spiral and the long burner. Any such iodine is driven by careful heating into the spiral part of the tube to be absorbed in the caustic solution.

The burners are then extinguished and the tube allowed to cool in the stream of oxygen.

For reception of the washings from the combustion tube, 10 ml. of the 20 per cent. aqueous sodium acetate solution are pipetted into a 100 ml. bottle or conical flask fitted with a ground-glass stopper. For rinsing the tube, 8 ml. of the sodium acetate solution in glacial acetic acid are brominated in a test tube by adding 2 to 3 drops of bromine.

The boat and platinum contacts are taken out of the cooled combustion tube, the brass tubes taken from it and the combustion tube taken off its stand. While holding it on the slant in one hand, the outside of the tube is wiped in the upward direction by means of a small clean towel. The solution of brominated acetate in glacial acetic acid is poured in 2 portions of 4 ml. each down the tube, catching the liquid in the bottle containing the acetate solution. The first portion is allowed to drain out before the second portion is poured down the tube. Then 3 portions of about 6 ml. of water are poured down the tube, allowing each portion to drain similarly before adding the next portion, and catching the water in the bottle. While pouring the wash liquids down the tube, it is advisable to rotate it so that all parts of the internal wall of the tube are washed.

Before the titration is made, the bromine in the solution is destroyed by allowing 4 to 5 drops of formic acid to run down the wall of the bottle into the solution and shaking it carefully. The absence of free bromine is first tested by the smell of the solution and then by adding a very small drop of methyl red suspended on a glass thread. If the indicator is decolorised, bromine is still present and 1 drop more of formic acid is added. The testing and addition of formic acid is continued until the indicator remains slightly pink. Then 4 ml. of the 10 per cent. potassium iodide solution and 10 ml. of 2 N sulphuric acid solution are added and the solution allowed to stand for 10 minutes with the bottle stoppered. The liberated iodine is titrated rapidly with 0·025 N sodium thiosulphate solution to a slightly yellow colour, about 1 ml. of starch solution added and the titration continued to a slightly pink end point due to the presence of methyl red. A macroburette may be used.

Calculation.—1 ml. of 0·025 N sodium thiosulphate solution is equivalent to 0·529 mg. of iodine. Hence, if V ml. of sodium thiosulphate, of a normality n with respect to 0·025 N, are used in the titration of the solution given by a weight w mg. of material, the percentage of iodine is given by:

$$\text{Per cent. iodine} = 52{\cdot}9\ nV/w.$$

CHAPTER X

DETERMINATION OF PHOSPHORUS

THE compound is oxidised by means of a mixture of sulphuric and nitric acids, the phosphorus in it being converted to phosphoric acid. This acid is precipitated as a complex cobalt-molybdophosphate and weighed as such.

REAGENTS

Nitratopentammine-cobaltinitrate (*Jörgensen's salt*).—This complex salt, of the formula $[Co(NH_3)_5\ NO_3]\ (NO_3)_2$ is prepared by Jörgensen's method (31). 32 gm. of cobalt nitrate hexahydrate are dissolved in 20 per cent. nitric acid and 200 ml. of concentrated ammonia added. The mixture is heated to boiling and 14 gm. of iodine are added. After about 30 minutes, the iodine dissolves, leaving a brown-yellow crystalline precipitate. The mixture is cooled and then the precipitate filtered off. Solid ammonium nitrate is added to the red filtrate. If a precipitate appears, the solution is again filtered. 16 N nitric acid is then added to the filtrate until a precipitate forms, after which a further 500 ml. of the acid are added. The mixture is heated on a water bath for about 3 hours. After cooling, it is filtered and washed first with dilute nitric acid and then three times with alcohol. The precipitate is finally washed with cold water until the washings give no precipitate with sodium pyrophosphate. The reagent solution is a solution of 8·5 gm. of this salt in 1 litre of warm distilled water at 40° C., which is stirred well during the dissolution. The solution is cooled, filtered and stored in a glass-stoppered bottle.

Acid sodium molybdate.—A quantity of pure molybdic acid is ignited at dull red heat and then repeatedly evaporated with concentrated nitric acid until a light yellowish-green product is obtained. This product is dissolved in the minimum amount of freshly-prepared 10 per cent. caustic soda solution. The solution is just acidified with dilute sulphuric acid, filtered and made up to 500 ml. The solution should be colourless or have only a faint yellow tinge.

Nitric acid solution, 0·3 N.

Ethyl ether (Anhydrous—M.A.R. grade).

Absolute alcohol (A.R. grade).

METHOD

20 to 25 mg. of the substance are accurately weighed on a counterpoised glass scoop and quantitatively transferred to a clean Pyrex

boiling tube 10 cm. long and 3 cm. diameter. It is important that before use the test tube should have been thoroughly cleaned with chromic-sulphuric acid solution (p. 32), washed and dried. The tube should have marks to indicate 5 ml. and 18 ml. capacities. To the substance 2 ml. of concentrated sulphuric acid and 1 ml. concentrated nitric acid are added and the mixture boiled over a micro-flame, preferably on a digestion stand, until fumes of sulphur trioxide appear. 1 ml. of concentrated nitric acid is then added and the boiling again continued until fumes appear. This process is repeated once more. If the solution is still not clear, a few drops of 30 per cent. hydrogen peroxide are added and the mixture again heated until fumes appear. If the solution is still not clear, the addition of hydrogen peroxide and heating is repeated until it is. Finally, 1 ml. of water is added and the mixture heated until fumes appear. The tube is cooled and its contents diluted to 5 ml. To the solution approximately 1 ml. of molybdate reagent is added for each mg. of phosphorus present and the solution heated to 90° C. in a beaker of water. Sufficient of Jörgensen's salt solution is then added to colour the supernatant liquid pink and then 3 to 5 ml. in excess. If the solution is now greater than 18 ml., it should be evaporated to this volume. The solution is stirred and kept at 90° C. for about 10 minutes. If less than 2 mg. of phosphorus is present, the precipitate forms slowly and the sides of the tube should be scratched with a glass rod. If the amount of Jörgensen salt required for the precipitation is large, a pink precipitate may form which requires longer digestion. The solution is then cooled and filtered by Pregl's method on a weighed sintered glass filter tube padded with medium-fibred asbestos 0·5 to 2 mm. thick. The filter is prepared in the following manner: The filter tube is placed in the filtration apparatus (p. 35) and a 2 mm. layer of medium Gooch-crucible asbestos filtered upon the sintered glass plate and evenly pressed together with a sharp-edged glass rod. The pad is washed with 0·3 N nitric acid, then with three 5 ml. portions of alcohol and finally, twice with ether in 5 ml. portions. An air filter is placed in the orifice of the tube and air drawn through it for 5 minutes. The tube is then wiped with chamois leather, placed in a desiccator over calcium chloride for 30 minutes and weighed in the usual manner.

For the filtration of the precipitate in the test tube, the prepared filter tube is again placed in the filtration apparatus, the test tube containing the precipitate connected by siphon tube with the top of the filter tube, and the suction to the filter flask turned on and adjusted, so that approximately 2 drops flow upon the filter mat per second. The precipitate is first washed with 0·3 N nitric acid to free it from sulphuric acid, then once with a small amount of water, then with three 5 ml. portions of alcohol and finally with two 5 ml. portions of ether. The

filter is partially dried, as during its preparation, by drawing air through it for 5 minutes after detaching the siphon tube and closing its orifice with an air filter. The drying is completed by cleaning the tube with chamois leather and allowing it to remain over calcium chloride in a desiccator for 30 minutes. After this time it is weighed as before, the increase in weight being the weight of the precipitate.

The precipitate is removed from the filter after each determination. It is most easily removed by drawing strong caustic soda through it, washing the residue with water and dissolving it in hot nitric acid.

Calculation. The precipitate being nitratopentammine-cobaltidodecamolybdophosphate of the formula $[Co(NH_3)_5 NO_3] H_3PMo_{12}O_{41}$ and the theoretical factor being applicable, the weight of phosphorus is 0·01515 times the weight of precipitate. Hence, if, in analysing m mg. of material, w mg. of precipitate are obtained, the percentage of phosphorus is given by:

$$\text{Per cent. phosphorus} = 1{\cdot}515\ w/m.$$

CHAPTER XI

DETERMINATION OF ARSENIC

THE organic material is oxidised with a mixture of sulphuric and nitric acids in a Kjeldahl digestion flask; the arsenic acid so formed is treated with potassium iodide and the liberated iodine titrated with a standard solution of sodium thiosulphate.

REAGENTS

Dilute sulphuric acid.—30 per cent. solution of concentrated acid in water.

Nitric acid.—Concentrated solution.

Hydrogen peroxide.—100-vol. strength M.A.R. grade.

Hydrochloric acid, free from chlorine.—To free the acid from chlorine, about 30 ml. of the concentrated acid is boiled gently for 2 minutes in a 100 ml. conical flask with a ground-glass stopper. After the boiling, the stopper of the conical flask is at once inserted and the flask cooled under the water tap.

Potassium iodide solution, 10 per cent. solution.—The solution must be prepared fresh and should be colourless.

Standard sodium thiosulphate solution, 0·025 N.—For preparation and standardisation, see Appendix II.

Starch indicator (p. 110).

METHOD

30 to 50 mg. of substance are weighed accurately on a counterpoised glass scoop and transferred to a dry Kjeldahl flask. Any material sticking to the neck of the flask is rinsed down into the bulb with 3 ml. of 30 per cent. sulphuric acid. After adding 0·5 ml. of nitric acid, the flask is heated over a small flame, by itself, or on a digestion stand if a number of determinations are to be made. When white fumes of sulphur trioxide appear, another 0·5 ml. of nitric acid is added and the heating repeated until the fumes reappear. Finally, 0·5 ml. of hydrogen peroxide is added and the solution again heated. This process is repeated until on cooling the flask after the fumes appear the solution is clear. At this stage the hydrogen peroxide is destroyed together with excess oxypersulphuric acid, by treating the solution twice or thrice with 1 ml. of distilled water and heating after each addition until

the fumes of sulphur trioxide appear and sulphuric acid condenses on the wall of the flask. Finally, 1 ml. of distilled water is added and the contents of the flask boiled for a few seconds. The contents of the flask are transferred to a 100 ml. conical flask provided with a ground-glass stopper. The digestion flask is rinsed with 5 ml. of boiled, concentrated hydrochloric acid in 2 to 3 portions to transfer the solution quantitatively to the conical flask.

For estimating the arsenic acid, 2 ml. of a 10 per cent. solution of potassium iodide are added to the solution in the conical flask which is then stoppered and allowed to stand for 10 minutes. The liberated iodine is then titrated with 0·025 N sodium thiosulphate solution using a micro-burette for the titration. When the iodine colour has been nearly discharged, the liquid is diluted to 40 ml. with boiled distilled water, about 2 ml. of starch indicator solution added and the titration completed to an end point of a faint reddish tint; the blue colour reappears only after 5 to 10 minutes.

Calculation.—As 1 ml. of 0·025 N sodium thiosulphate is equivalent to 0·937 mg. of arsenic, then if V ml. of the sodium thiosulphate solution, of a normality n with respect to 0·025 N, are used in the titration of a solution given by w mg. of compound taken for analysis, the percentage of arsenic is given by:

$$\text{Per cent. arsenic} = 93{\cdot}6\ nV/w.$$

Blank test.—Though boiled solutions are used, a small amount of iodine is usually obtained from oxidation by air. Before a series of determinations is made, a blank titration of the reagents should therefore be made as follows: To 3 ml. of 30 per cent. sulphuric acid in a test tube, 3 ml. of distilled water are added, the mixture boiled and rinsed into a conical flask provided with a ground-glass stopper, by means of 5 ml. of boiled, concentrated hydrochloric acid. To this solution are added 2 ml. of a 10 per cent. potassium iodide solution; the flask is stoppered and allowed to stand for 10 minutes. The solution is then diluted with 40 ml. of distilled water, 2 ml. of starch indicator solution are added and the solution titrated to a faint reddish colour with 0·025 N sodium thiosulphate solution. The volume of any thiosulphate solution used in this blank titration must be deducted from the volume of the solution used in an analytical titration.

CHAPTER XII

CARBOXYL GROUP : DETERMINATION OF NEUTRALISATION EQUIVALENT

The neutralisation equivalent of an acid is the amount of the acid which is required to neutralise 1 litre of normal alkali solution. If the acid is monobasic, this amount in grammes is the same as the molecular weight. If the acid is polybasic, the amount in grammes is a sub-multiple of the molecular weight. The equivalent is determined by titrating about 20 mg. of the organic acid with 0·025 N sodium hydroxide solution. Certain precautions have to be observed. To prevent absorption of carbon dioxide by the solution, thus affecting the end point of the titration, the solution is boiled just before bringing the solution to neutrality. To inhibit the dissociation of the sodium salt formed during the course of the titration, alcohol is added to the solution.

APPARATUS

Micro-burette.—The micro-burette has been described earlier (p. 31).

REAGENTS

Standard hydrochloric acid solution, 0·025 N.—For preparation, see Appendix II.

Standard sodium hydroxide solution, 0·025 N.—For preparation, see Appendix II.

Neutral ethyl alcohol, 50 per cent. solution.—100 ml. of 95 per cent. ethyl alcohol is diluted with 100 ml. distilled water ; two drops of indicator are added, the solution boiled for 30 seconds and then titrated to the slightly pink colour. The neutralisation should be repeated if the solution has stood several weeks.

Phenolphthalein indicator, 1 per cent. solution.—0·1 g. of solid indicator is dissolved in 100 ml. of absolute alcohol.

METHOD

About 20 mg. of substance are weighed accurately in a charging tube and transferred to a Pyrex conical flask, which has been cleaned, steamed out and cooled. The material is dissolved in about 10 ml. of

50 per cent. neutral ethyl alcohol, if necessary by warming the solution, and then titrated with the standard solution of sodium hydroxide until the end point is nearly reached, that is, until the pink colour of the alkaline indicator persists a little while and only just disappears on shaking the solution. The solution is now boiled for 20 seconds to expel any carbon dioxide absorbed from the air and then rapidly titrated to the end point, which is shown by a permanent pink colour. If the end point is passed, the standard hydrochloric acid solution is added in slight excess, the solution boiled again for a few seconds and then titrated back. Corrections for any inexactness of the normality of the solutions must be applied, of course, in the calculations.

Calculation.—The neutralisation equivalent is given by:

$$\text{Equivalent} = \frac{\text{mgm. of substance} \times 40}{\text{ml. } 0{\cdot}025 \text{ N NaOH}}$$

CHAPTER XIII

DETERMINATION OF ALKOXYL GROUPS

The principle of the Zeisel method of determining methoxyl and ethoxyl groups is to decompose the group with boiling hydriodic acid, which leads to the formation of the alkyl iodide. The volatile iodide is swept in a current of carbon dioxide into a receiver, in which is a solution of sodium acetate in acetic acid, to which bromine has been added. The iodide is oxidised thereby to iodine monobromide which is further oxidised to iodic acid. The iodate formed is titrated, after decomposing it by the addition of potassium iodide to the solution, by means of sodium thiosulphate solution.

APPARATUS

The carbon dioxide for flushing the apparatus is generated in a Kipp generator. The outlet of the Kipp is attached through a wash bottle containing sodium carbonate solution (to entrap hydrochloric acid vapours) to the side arm, A, of the reaction apparatus shown in Fig. 22. On the rubber tubing leading from the wash bottle to the inlet of the reaction apparatus is a screw-clamp for regulating the flow of the carbon dioxide.

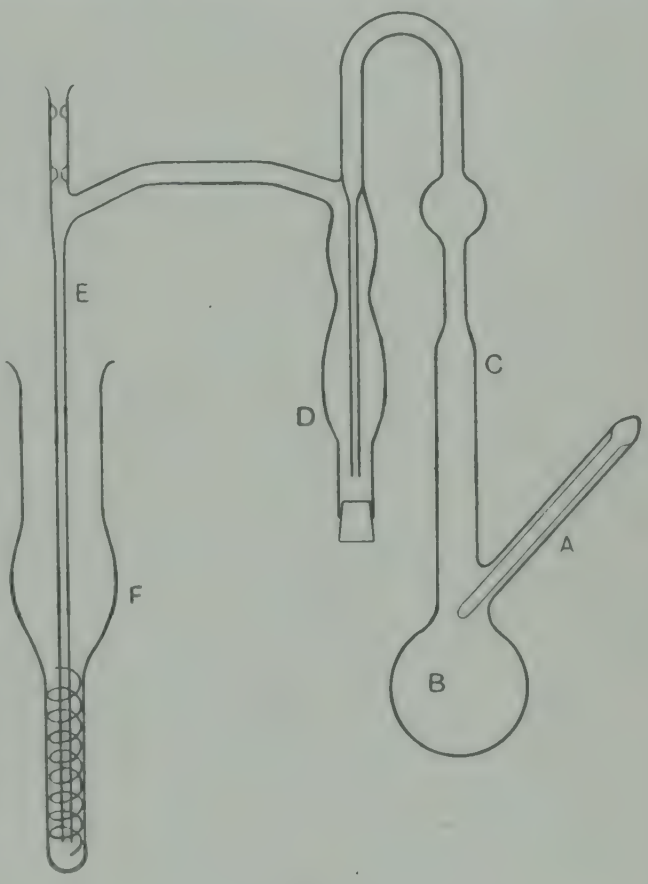

FIG. 22.

The reaction apparatus is made of Pyrex glass. It consists of a small round-bottomed flask, B, of 25 ml. capacity provided with the side arm A and the vertical ascension tube, C. The side arm A not only functions as inlet for the carbon dioxide but also for introducing the sample into the bulb. To prevent escape of vapours into A from the boiling

flask during the reaction, a loosely-fitting glass rod is inserted into it; a collar near its upper end prevents it slipping down the arm into the flask.

The ascension tube from the boiling flask is of 7 mm. internal diameter and has a length of 16 cm. up to the bend at the top. The tube bends over and descends to form the washer D 7 cm. in length and 1·5 cm. diameter at its widest part, which is sealed upon it. The washer is open at the bottom, but is normally closed by means of a rubber stopper. A side arm from the washer is bent to the shape shown, giving an overall length of 9 cm., and is connected to the outlet tube, E, which is open at both ends. This tube is 27 cm. long and is made of tubing of 2 mm. bore. The side arm from the washer meets it at a point 4 cm. below the top. The tube has two constrictions near the top, at the positions indicated. The tube is sealed by putting a small drop of water into it; the constrictions hold this drop. This water seal is impermeable to alkyl iodide vapour. A small rubber stopper in the top of the tube completes its sealing.

The tube dips into the receiver F. This receiver has an internal diameter for its upper length (which is 4·5 cm.) of 1·8 cm. and is expanded into a bulb of 3 cm. diameter. The lower tube of the receiver is 6·5 cm. long and of 1 cm. internal diameter. In order to lengthen the track of the gas bubbles through the liquid in this receiver, a glass spiral, making a fairly close fit, is placed within the annulus between the receiver and the inner tube E. A mark on the wall of the receiver at a level equivalent to a capacity of 10 ml., with the inner tube and spiral inserted, is useful.

REAGENTS

Hydriodic acid, density 1·7.—The M.A.R. grade of acid should be used. It should be stored out of contact with air and kept from exposure to light, both of which cause its decomposition to iodine. It is best to order the acid in small amounts so that when used it is reasonably fresh. Results tend to be low if acid which has suffered decomposition is used, because of the weakness of the acid.

Acetic anhydride, M.A.R. grade.

Sodium thiosulphate solution, 5 per cent. solution in water.

Sodium acetate solution in glacial acetic acid, 20 per cent. solution.

Bromine, M.A.R. grade, free from iodine.

Formic acid, 80 to 100 per cent. strength.

Potassium iodide solution, 10 per cent. concentration in water.

Standard sodium thiosulphate solution, 0·025 N strength.—For preparation, see Appendix II.

Starch indicator solution (p. 110).

METHOD

Preparation of the apparatus.—Before each analysis the apparatus is cleaned and dried as follows: The delivery tube is cleaned of grease by immersing it in warm chromic-sulphuric acid (p. 32) for 10 minutes. The inlet tube to the reaction flask is then connected to a suction pump and 400 ml. of tap water, followed by 200 ml. of distilled water, are drawn through the apparatus by way of the delivery tube. The apparatus is then wiped on the outside and dried internally by heating it in an air oven at 120° C.

One ml. of a suspension of red phosphorus in water is introduced into the washer, which is then stoppered. The delivery tube is rinsed down inside and out, first with distilled water and then with alcohol. A drop of distilled water is introduced into it through its upper orifice to form the water seal at the constriction and the stopper inserted. The apparatus is loosely suspended from a clamp so that the boiling flask is about 2 cm. above the micro-burner.

The receiver and spiral in it are washed with tap water, followed by distilled water and alcohol. 10 ml. of the solution of sodium acetate in glacial acetic acid are introduced into it, followed by 10 to 12 drops of bromine. The receiver is then put in place round the delivery tube. It is suitably supported on a block of wood. The spiral should fit fairly closely to the delivery tube on the one hand and the receiver on the other, so that the bubbles ascend round the spiral.

Analysis.—The material to be analysed is weighed accurately in a tinfoil cup. To prepare this cup, the foil is cut to the size of about a shilling and this piece formed into a cup by moulding it round the smoothed end of a glass rod. After weighing the material into the cup, the open end is pinched to close it and the capsule thus formed is introduced into the reaction flask through its side arm. To the material in the flask are added a few crystals of phenol (sufficient to cover the end of a micro-spatula) and 5 ml. of hydriodic acid.

When the materials have been added, the choking tube for the side arm is inserted into it and the rubber tubing leading to the Kipp generator slipped over the end of the side arm. With the screw-clamp on this tubing closed, the tap on the Kipp generator is turned on and the screw-clamp carefully opened so that never more than two bubbles rise through the liquid in the receiver at the same time.

The heating of the reaction flask is then begun with a very small non-luminous flame on the micro-burner; a chimney on the burner

is useful to prevent draughts from disturbing the flame. As the flask is heated, the rate of passage of the gas through the receiver is accelerated, but the gas rate should not be changed, for, when the liquid boils, the normal rate is resumed. The liquid is boiled for 30 or 40 minutes.

When boiling is complete, the receiver is lowered away from the delivery tube and the delivery tube rinsed well, inside and out, with distilled water which is caught in the receiver. The contents of the receiver are rinsed quantitatively into a 100 ml. conical flask with a ground-in stopper already containing 10 ml. of a 20 per cent. aqueous solution of sodium acetate. Two drops of formic acid are added to the flask and the flask shaken, with addition of more formic acid if necessary, until the solution is colourless. About six drops of formic acid should suffice to destroy the bromine. That the bromine has been destroyed may be verified either by the lack of smell of free bromine or more positively by adding a small drop of methyl red indicator (p. 89) from a glass thread; the presence of bromine decolorises the indicator; further drops of formic acid are added with shaking of the flask until the indicator is no longer decolorised.

Five ml. of a 10 per cent. solution of potassium iodide in water are added and the solution acidified with 10 ml. of 2 N sulphuric acid. After allowing the flask to stand stoppered for 5 minutes, the liberated iodine is titrated with 0·025 N sodium thiosulphate solution. The first part of the titration is done rapidly to a faint yellow colour of the iodine. Then about 1 ml. of starch solution is added and the titration completed to the discharge of the blue colour of the starch iodine complex.

Calculation.—As 1 ml. of 0·025 N sodium thiosulphate corresponds to 0·129 mg. of methoxyl, the percentage of methoxyl in the compound is given by: Per cent. methoxyl $= 12{\cdot}9\ N\ V/w$ where N is the normality of the sodium thiosulphate solution with respect to 0·025 N, V is the ml. of thiosulphate used in the titration and w is the weight, in mg., of material used.

CHAPTER XIV

DETERMINATION OF ACETYL GROUP

THE acetyl group is saponified with a suitable reagent, a normal solution of potassium hydroxide in ethyl alcohol, the reaction mixture diluted with magnesium sulphate solution, acidified with sulphuric acid and the liberated acetic acid distilled. The distilled acid is then titrated with a standard solution of alkali. The method, due to Clark (12), is primarily designed for O-acetyl compounds, but by saponifying with a solution of potash in n-butyl alcohol, it can be extended to N-acetyl compounds.

APPARATUS

The hydrolysis is done in a 50-ml. flask A (Fig. 23). The flask is closed by a ground-glass stopper through which passes a tube B of

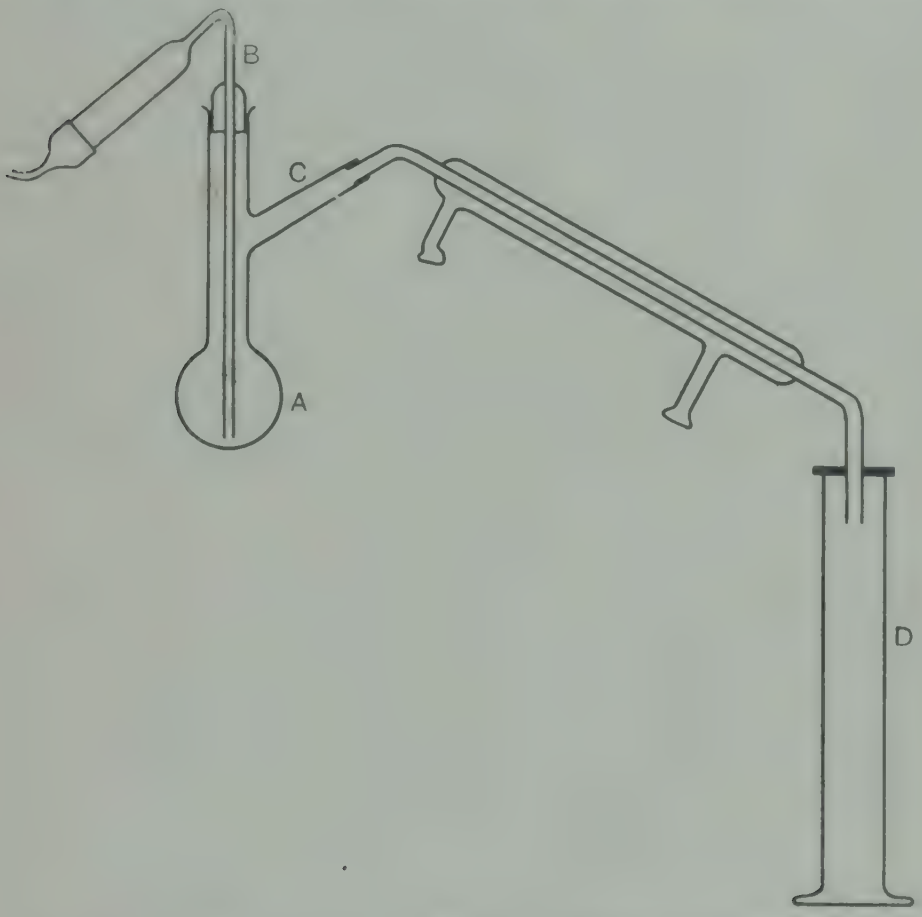

FIG. 23.—APPARATUS FOR THE DETERMINATION OF ACETYL GROUPS

4 mm. internal diameter, expanded, at the part which is bent over outside the flask, to a diameter of 8 mm. The end of this part of the

tube is attached by rubber tubing to a round-bottom flask of about 2 litres capacity (not shown) in which steam is generated. The tube B extends nearly to the bottom of the reaction flask. The flask also has a side arm C, bent upwards, of 8 mm. diameter and 5 cm. long, ending in the female part of a ground-glass joint. The male part of the joint is the end of a condenser of the shape shown. The condenser is rotated round this joint to the vertical position to serve as a reflux while the reaction is proceeding or to the sloping position to serve as the conventional condenser for the distillation. The condenser jacket is 16 cm. long. The distillate is collected in a 100 ml. measuring cylinder D.

REAGENTS

Potassium hydroxide solution in 95 per cent. ethyl alcohol, 1 N.—5·7 gm. of potassium hydroxide are dissolved in 100 ml. of 96 per cent. ethyl alcohol.

Potassium hydroxide solution in n-butyl alcohol, 1 N.—For the estimation of the acetyl group in N-acetyl compounds a normal solution of potash is made in n-butyl alcohol.

Magnesium sulphate solution.—100 gm. of magnesium sulphate and 1·5 gm. of concentrated sulphuric acid are dissolved in sufficient water to make 180 ml. of solution.

Standard potassium hydroxide solution, 0·02 N.—For preparation and standardisation, see Appendix II.

Phenol red indicator solution.—0·1 g. of the indicator is rubbed in an agate mortar with 2·85 ml. of 0·1 N sodium hydroxide solution and the mixture made up to 100 ml. with distilled water.

METHOD

About 20 mg. of the sample are weighed accurately on cigarette paper and placed with the paper in the distilling flask A. Two ml. of the normal potassium hydroxide solution in alcohol are added and with the condenser in the vertical position as a reflux the liquid is heated to boiling or until all the sample is dissolved. After 4 minutes further heating 18 ml. of the magnesium sulphate solution are added. The condenser is then rotated round the ground-glass joint to slant downwards so that its exit end lies over the receiver D. Steam is then generated in the generator and passed through the apparatus, while the flask A is heated with a small flame so adjusted that the volume of liquid is reduced to about 15 ml. while 50 ml. of distillate are collected. (The analyst will be helped by a few prelimin-

ary blank experiments to familiarise himself with this rate of distillation.) Under these conditions, the whole of the acetic acid is found in the distillate. This volume of distillate is titrated with the 0·02 N solution of potassium hydroxide, using phenol red as indicator, to the appearance of the red colour.

During the course of a series of acetyl determinations, it is advisable to check the standardisation of the 0·02 N potassium hydroxide solutions frequently.

The method may be applied to some N-acetyl compounds by using the following modification: The sample in the distillation flask is dissolved in 2 ml. of a normal solution of potassium hydroxide in n-butyl alcohol. The mixture is refluxed for an hour and the above procedure then followed.

Calculation.—One ml. of exactly 0·02 N-potassium hydroxide is equivalent to 0·86 mg. acetyl. If w mg. of material are analysed and V cc. of alkali are used for titration, n being the determined normality relative to 0·02 N,

$$\text{Per cent. acetyl} = 86\ Vn/w.$$

CHAPTER XV

DETERMINATION OF DENSITIES OF LIQUIDS

A KNOWN volume of liquid is weighed in a capillary-tube pycnometer. The density is given directly from the value of the weight and volume, after making the customary corrections for air buoyancy.

APPARATUS

Pycnometer.—A suitable pycnometer, recommended by Furter (29), is shown in Fig. 24. It is best made from Jena glass. It is of capillary

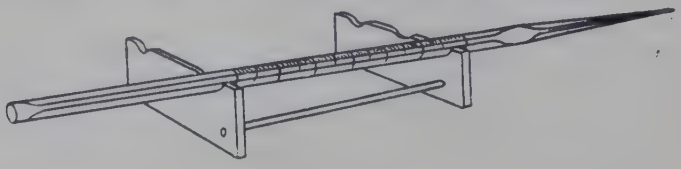

FIG. 24.

tubing of 1 mm. bore and 6 mm. external diameter and is 12 cm. long. The capillary bore should be as uniform as possible, so that each division of the graduations represents as nearly as possible a constant volume. This is desirable, though not absolutely essential ; the volume of the pycnometer along the graduated part must be calibrated. To have a very uniform bore does, however, eliminate rather tedious corrections for the volume.

One end is drawn out and the point is ground so that the wall of the capillary is fine at the tip. The other end of the tube is splayed out as shown. An expansion at the point shown is an advantage in filling the tube.

The graduations, uniformly made along the length of the tube, are spaced 1 mm. apart. Every fifth graduation should preferably extend over half the circumference and every tenth graduation over the whole circumference.

METHOD

Before use, the tube is cleaned by drawing chromic-sulphuric acid (p. 32) into the capillary, allowing the acid to remain there for half an hour or so, draining the tube and then washing it with tap water, distilled water and finally acetone. The exterior is washed with water and acetone. The tube is finally dried by drawing air through it, the air being warmed by passage through a bunsen flame. From this point onwards, the tube should be handled only with chamois finger-tips or gloves.

After drying, the wide opening of the tube is wiped out with a small wad of cotton wool fixed to a piece of steel wire. The outside of the tube is wiped with moist flannel and dried by two wipings with chamois

leather, in the same way as the absorption tubes for the carbon and hydrogen determination (p. 58). It is then laid on the support shown in Fig. 24, and placed in the balance-case.

In 20 to 30 minutes it will have come to temperature equilibrium with the balance. It is removed from its support by means of the weighing fork and placed on a suitable support on the balance-pan. (The support used for the carbon-hydrogen absorption tubes (p. 23) will serve for this purpose.) The pycnometer is counterpoised by means of a small glass flask filled with lead shot.

Calibration.—The volumes represented by the graduations must first be determined. This is done by weighing the water occupying the pycnometer up to various graduations. The pycnometer is filled as follows: After the empty tube has been weighed, it is removed, wiped with a piece of chamois leather and a clean piece of rubber tubing fixed over the end. The point is then immersed in distilled water and the water drawn up to as near the upper graduation as possible. The tube is at once placed in the horizontal position, again wiped with chamois leather, placed in its support and taken to the balance-case. A thermometer, which can be read to 0·1° and has been calibrated to this accuracy, is placed on the support so that its bulb lies close to the pycnometer. After it has come to temperature equilibrium, the level of the water in the capillary is read, preferably with a lens, and the temperature on the thermometer read to 0·1°. The pycnometer is then weighed at once.

The process is repeated by filling the tube to about every tenth graduation. The calculations of the volume are made with corrections for the errors due to air buoyancy. The weight of water, m, filling the tube to the graduations as read is the difference between the weights of the filled and unfilled pycnometer. If d_W is the density of water at the experimental temperature, d_A the density of air, which may be taken as 0·0012 and d_B the density of the weights (e.g., 8·4 for brass weights, 21·4 for platinum weights), the volume is given by

$$V = \frac{m}{d_W}\left(1 + \frac{d_A}{d_W} - \frac{d_A}{d_B}\right)$$

The same calculation for the different weights of water filling the pycnometer to different graduations enables the calibration curve of the volume of the pycnometer to these graduations to be drawn.

In determining the density of any other liquid, the pycnometer is filled with it (preferably to near the top mark), wiped, allowed to gain temperature equilibrium with the balance, the volume of liquid in it read from the graduation at which the meniscus lies, the temperature taken and the pycnometer weighed. The correction for the buoyancy error is again applied to the weight of the liquid in calculating the density.

CHAPTER XVI

DETERMINATION OF MELTING-POINT AND BOILING-POINT

THE melting-points of materials are commonly determined on micro-amounts of the material and the principle of the method described below is well known to the chemist. We have, however, thought it advisable to describe the apparatus and method in some detail. Thermometric corrections have to be applied to the reading of the melting-point, the magnitude of the correction depending on the thermometer and on the apparatus. The apparatus should be fairly rigorously specified so that a given set of corrections may hold. Mulliken's specification (15) of the apparatus is given in this chapter and it is to this specification that the corrections for the observed melting-points, which are tabulated after the description, apply.

For the boiling-point determination, two methods are described, the simple and elegant Emich method (14) and the Siwoloboff (15). Both are much quicker than the macro-method of distilling the material, and are as accurate.

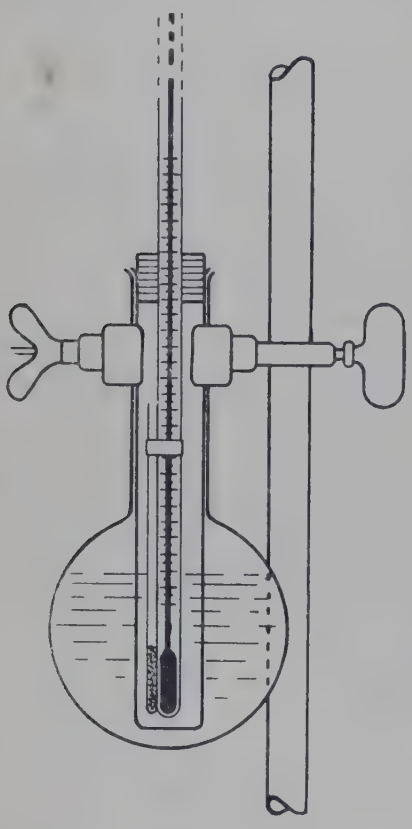

FIG. 25.

A. DETERMINATION OF MELTING-POINT

A suitable apparatus for the determination of the melting-point is shown in Fig. 25. It is advisable to have two sets of apparatus, one for low and the other for high temperatures. The apparatus has the advantage that, in being virtually closed, free escape of fumes from the liquid bath at high temperatures is prevented, and dust cannot enter the bath, so that its frequent renewal is not necessary.

The flask of the apparatus is round-bottomed with a capacity of about 200 ml.; its bulb is 6·5 cm. in diameter and the neck is 7·5 cm. long and 2 cm. diameter. The inner test tube has a diameter of 1·5 cm. and hangs freely from the lip of the flask. Both the inner tube and flask are filled with a suitable clear liquid to the level indicated; the test tube should not be used as an air bath.

The best liquid bath for temperatures up to 200° is colourless concentrated sulphuric acid. It becomes brown rather quickly through contact with organic material and has to be renewed, therefore, fairly often. For temperatures above 200° (and for those below also) a suitable bath is a mixture of concentrated sulphuric acid and potassium sulphate or potassium hydrogen sulphate. The bath is prepared by heating together concentrated sulphuric acid and potassium sulphate in the proportions of 70 parts to 30, or the acid and potassium hydrogen sulphate in the proportions of 55 parts to 45, in a porcelain dish until boiling ceases at 320° C. The mixture has the fluidity of glycerine; this mixture is less corrosive and less easily discoloured by organic material than sulphuric acid. This mixture tends to become pasty through exposure to air, because of absorption of water, but it is easily liquefied again by heat. When the melting-point exceeds 300° and the apparatus has not been heated above 250° for some weeks, the bath should first be boiled for a few minutes; if this is not done, the steam given off at about 300° will cause bumping and interfere with observations. Should the mixture solidify to a hard mass a short boiling brings it back to its normal state.*

The melting of the material is observed in a thin-walled glass capillary sealed at the lower end and containing a few crystals of the material. These tubes are 6 to 7 cm. long and have an internal diameter of 1 mm. They are best made from soft glass tubing with an internal diameter of at least 1 cm. The tubing is rotated in the hands while being heated in the blowpipe flame towards the centre so that a length of about 2 cm. becomes dull red. The tube is withdrawn from the flame and drawn out rather slowly until the heated part is about $\frac{1}{2}$ metre long; the diameter of the capillary portion will then be approximately 1 mm. Lengths of 12 cm. are cut off and each of these lengths made into two capillary tubes by heating the length at the centre so that it collapses and drawing out the tubing. The very fine lengths of capillary left on the main capillary are fused off by heating.

To charge the capillary, its open end is forced down into a small heap of the finely powdered material. The tube is inverted so that the open end with its plug of powder is uppermost and the flat side of a file is drawn horizontally across the tube just below the plug of powder. The powder, loosened by the vibrations set up in the glass, falls to the bottom of the tube to a depth of about 1 mm. The capillary is now attached by wiring it with platinum wire to the thermometer. The wire should be about 2 cm. above the surface of the bath and the substance in the capillary should be opposite the middle of the thermometer bulb. A simple alternative to this method of attachment is to attach a piece of glass rod to the thermometer by fine platinum wire, the end of the glass rod being at the same level as the bottom of

* Dibutyl phthalate is also a suitable liquid for the bath.

the thermometer bulb, and to press the capillary tube in the crotch between the two. The capillary adheres firmly to the rod and thermometer and needs no wire attachment to the thermometer.

The thermometer should be one reading from up to 360° C., of a diameter of about 5 mm. and a length per degree reading of about 0·85 mm. For the application of the correction table given below, the thermometer should be so arranged in the tube that its 10° C. mark is on the level of the liquid and 100° above that should be within the tube.

The correct rate of heating the bath depends on the behaviour of the substance, but in general the heating rate should not exceed 2° C. per minute when within about 10° of the melting-point; otherwise, there may be some uncertainty that the thermometer and the bath are at the same temperature. A common practice in determining the melting-points of materials that fuse to mobile liquids is to observe the thermometer at the moment when the first clear drop appears, which is of sufficient size to detach itself from the solid mass and roll down the capillary under the influence of gravity. As observation at this moment gives values nearer the true melting-point than observation at either the moment of complete fusion, or at the moment of incipient fusion, with compounds that are not free from every trace of impurity, this method of observation is on the whole best suited for analytical use.

Correction table.—It is assumed that the thermometer itself has been corrected. The following corrections are those for the exposed stem. They are added to the observed value, which governs the value of the correction.

Observation, deg. C.	*50*	*60*	*70*	*80*	*90*	*100*	*110*	*120*	*130*	*140*	*150*	*160*	*170*
Correction, deg. C.	0·1	0·2	0·3	0·5	0·7	0·9	1·1	1·4	1·7	2·0	2·3	2·7	3·1
Observation, deg. C.	*180*	*190*	*200*	*210*	*220*	*230*	*240*	*250*	*260*	*270*	*280*	*290*	*300*
Correction, deg. C.	3·6	4·1	4·6	5·3	6·0	6·7	7·2	7·8	8·4	9·0	9·6	10·2	10·9

B. DETERMINATION OF BOILING-POINT

1. EMICH METHOD

Capillary tubes about 1 mm. in diameter are drawn from soft glass tubing as in the manner described under *Determination of Melting-Points* above (p. 129), but the tubing is cut off to a length of 20 cm. This piece is heated at the centre in the lowest part of the flame of a bunsen-burner until the glass just softens. The capillary is removed from the flame and the heated part quickly pulled to a fine capillary no wider than 0·1 mm. and about 10 or more cm. long. The fine capillary has about the right diameter if it can be bent into a loop without snap-

ping. The capillary is broken off at about 1 to 1·5 cm. from the point at which the wider capillary, which is about 10 cm. long, begins to taper to the narrow capillary. The end of the fine capillary is placed in the liquid, the boiling-point of which is to be determined and the liquid allowed to rise in it by capillarity until about 1 mm. of the wide part of the tube above the taper is filled. The capillary is withdrawn and the end of its fine tube sealed by holding it on a slant so that the end filled with liquid points upward and lies in the edge of the bunsen flame. In this position, gravity tends to pull the liquid from the point of the capillary as it is sealed in the flame and counteracts the capillary forces which hold the liquid at the point. It is indispensable that a small gas bubble should be left at the sealed end of the capillary tube below the liquid ; the bubble may occupy several millimetres of the fine capillary, but it should not extend into the tapered part of the tube. The position of the tube during the sealing causes the liquid to recede from the point and thus form the bubble of gas.

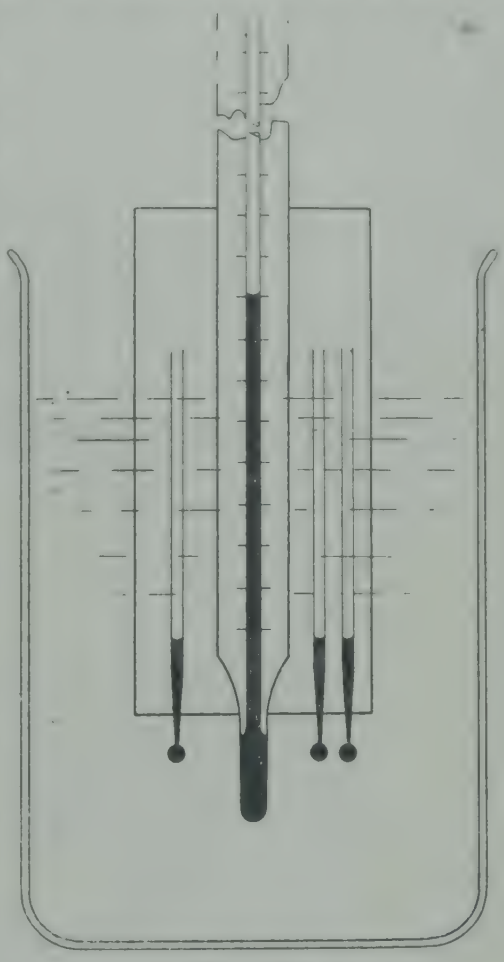

Fig. 26.

The heating bath may consist of a tall 250 ml. Pyrex beaker equipped with a glass stirrer composed of a long glass rod looped at the end. A cork is pushed over the upper end of the thermometer so that the thermometer may be held in a clamp on a retort stand, by means of the cork. A glass microscope slide is attached to the lower part of the stem of the thermometer by means of a rubber band, so that it lies behind the thermometer scale. About 150 to 200 ml. of a suitable liquid for the bath is poured into the beaker ; if a corrosive liquid such as sulphuric acid or sulphuric acid plus potassium sulphate is used, the rubber band should be placed appreciably above its surface. The capillary tube containing the test liquid is inserted between the rubber band and the slide so as to be held upright in the liquid close to, but to one side of, the thermometer. The bubble in the capillary tube should be level with the bulb of the thermometer. If necessary, other liquids in capillary tubes may be tested at the same time as shown in the figure (Fig. 26).

A fairly strong illumination, from a desk lamp close to the apparatus or a microscope lamp, is directed on to the capillary. The bath is heated rapidly at the start with continuous stirring of the bath until the temperature is about 10° C. below the boiling-point. (If the boiling-point is quite unknown, care will naturally be taken to minimise the period of rapid heating.) At this point, the bunsen-burner flame heating the bath is lowered to about 2 cm. and the stirring is done continuously throughout the depth of the bath. The thermometer is watched constantly and the flame heating the bath so regulated that the temperature rises about 0·5° per minute. The droplet in the capillary tube is now observed. When the droplet begins to quiver as the boiling-point is approached, the rate of stirring should be increased. The droplet then begins to rise in the capillary. When it just reaches the surface of the bath liquid, the flame is removed and the temperature, which is the boiling-point, is read. The bath is allowed to cool, the bath liquid still being stirred and the droplet allowed to fall to the tapered part of the capillary tube. The bath is again slowly heated and the boiling-point re-determined. In this way the determination may be repeated as often as desired.

FIG. 27.

2. SIWOLOBOFF METHOD

The following capillary tubes are required: (1) A capillary tube of 2 to 3 mm. diameter is drawn out from a piece of glass tubing of about 1 cm. diameter. The capillary tubing is sealed off in the flame so as to be about 6 to 7 cm. long. (2) A narrower capillary tube of about 1 mm. and about 10 cm. long which easily fits into the first tube is drawn to serve as a pipette. (3) A third capillary of the same diameter as the second is also needed to prevent superheating (Fig. 27). This last tubing is made by drawing out 1 cm. tubing to a diameter of about 1 mm., cutting off a length of about 20 cm. and heating this length at about 5 cm. from one end in the edge of the bunsen-burner flame until the walls fuse together. The tube is cut off below the fused part so as to leave about 3 mm. of the original tube at this end.

By means of the 1-mm. capillary about 3 drops of the liquid to be tested are inserted into the 2 to 3-mm. capillary tube which is then attached to a thermometer by a rubber band so that the liquid at the bottom of it is on the same level as the thermometer bulb. The thermometer is suspended in a heating bath in a flask or beaker. The very narrow capillary of 0·5 mm. diameter is dropped into the capillary so that the fused end is in the liquid.

The bath is gradually heated and the behaviour of the air bubbles

rising from the capillary tube in the liquid are observed. At first these bubbles emerge singly from the air confined below the seal in the narrower capillary, but a few degrees below the boiling-point there begins an apparently uninterrupted thread of small bubbles of vapour from it. The bunsen-burner heating the bath liquid is now removed until boiling stops and the liquid is seen to be about to recede into the chamber in the capillary. The temperature at which the liquid begins to recede is the temperature at which the liquid remaining in the tube would begin to boil.

CHAPTER XVII

DETERMINATION OF MOLECULAR WEIGHT

We describe three methods for determining molecular weights: the methods depending on the rise of the boiling-point and the lowering of the melting-point of a solvent, caused by a known concentration of the test material in the solvent, and the method of determining the vapour pressure of the material.

A. EBULLIOSCOPIC METHOD

The elevation of the boiling-point of a known pure organic solvent caused by a weighed amount of the test sample, the solute, with which it must not react, is determined by means of an accurate thermometer of the Beckmann type. Arrangements are made in the apparatus described (the Bobranski-Sucharda (1)) to ensure that the maximum temperature is constant.

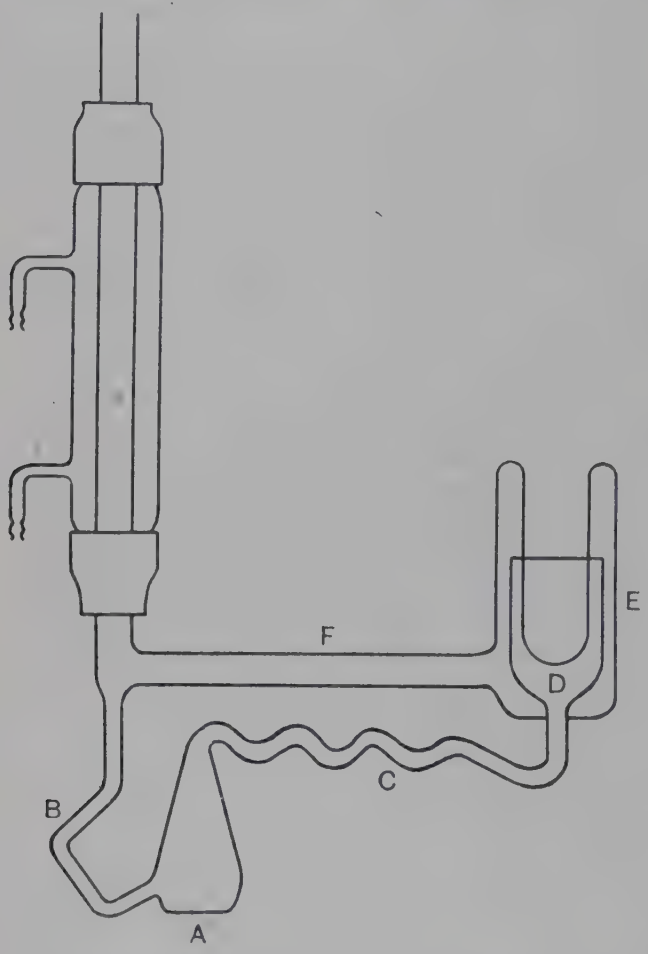

Fig. 28.—Apparatus for the Determination of Molecular Weights Ebullioscopically.

APPARATUS

The boiling-point apparatus is shown in Fig. 28. The boiler, A, of the apparatus has connected to it a siphon tube, B, and an upper side arm, C, bent in wavelike form as shown. The boiler, siphon tube and tube C are filled with the solvent, of which about 5 ml. are required. The other end of tube C is expanded to a cup, D, which forms a baffle within the double-walled thermometer cup, E. This thermometer cup is partially filled with mercury and holds the thermometer bulb, the mercury

ensuring good thermal contact between the boiling vapours inside the tube and the thermometer. An inclined tube, F, connects the interior of the cup with the top of the siphon.

The contents of the boiler are heated by means of a micro bunsen-burner provided with a chimney. The boiler stands on wire gauze while it is being heated. To ensure regular boiling of the contents of the boiler, powdered glass is sintered on the bottom of it. The vapour bubbles carry part of the liquid with them through tube C, in which the two phases come to temperature equilibrium. The liquid fills the internal cup, D, of the thermometer cup, overflows its rim and passes back through the connecting tube F to the siphon B and so back to the boiler. A water condenser sealed to the junction of the connecting tube and siphon prevents loss of solvent by evaporation.

It is important that a suitable solvent should be used. It must not react with the solute, the test material, and should not decompose at the boiling-point. Nor should the test material decompose at the boiling-point of the solvent. It should be easily soluble so that its solution and the final reading of the temperature of the solution should take no more than 2 to 3 minutes after dropping the test material into the solvent; if longer time is taken, the results may be uncertain through changes in the atmospheric pressure.

It is preferable to use two apparatus, the one as a " blank " apparatus, in which pure solvent alone is boiled, the other as the apparatus for the determination, in which the solution of test material in the solvent is boiled.

PREPARATION OF SAMPLE

Solids.—A solid is preferably used as a pellet which is prepared by compressing the material in a pellet press. About 20 mg. are used and are weighed in pellet form in a charging tube.

Liquids.—About 20 mg. of liquid are weighed accurately in a weighing capillary.

METHOD

A sheet of asbestos is arranged on the apparatus so that only the boiler and siphon of the apparatus are below it, the rest of the apparatus, including tube C, being protected by it from the heat of the flame. The mercury column of the micro-Beckmann thermometer is adjusted in height to the solvent used so that it is just above the zero mark when at the temperature of the boiling solvent. Five ml. (exactly measured) of the solvent are pipetted into the apparatus. The flame of the micro-burner is adjusted so that the liquid, when it boils, gently overflows the cup D and none of it tends to accumulate at the point where the tube C begins to widen to form the internal cup, D; any

accumulation of liquid at this point makes the circulation of solvent irregular. Conditions of boiling should become satisfactory in about 5 to 7 minutes, as the constancy of the thermometer—to 0·001° C.—should show. The thermometer is preferably read by means of a magnifying lens. The substance is now dropped through the condenser, G, to fall into the solvent. If the substance is a liquid, the tip of the capillary in which it has been weighed is broken off and both the capillary and its tip are dropped into the solvent. After 2 to 3 minutes, the thermometer reading should have again become constant, when it is again read. The difference in reading of the thermometer before and after introducing the solute gives the rise in boiling-point. If two apparatus are used, both are filled with 5 ml. of solvent, the solvent in each boiled and the readings of their thermometers taken after about 5 minutes. The weighed test sample is dropped in one apparatus and the reading of the thermometer in its apparatus taken 2 minutes later. The thermometer on the check apparatus should not have changed. If there is any change a corresponding correction should be applied to the elevation of the boiling-point.

The molecular weight, M, is given by:

$$M = 100\,Kw/WE$$

where K is the molecular constant of elevation of boiling-point of the solvent (see table below), w is the wt. of the sample, W is weight of solvent (volume × density) and E is the observed elevation of boiling-point.

Molecular Boiling-point Constants

Solvent.	*Boiling-point, deg. C.*	*Density.*	*Const. K.*
Acetic acid	118·1	1·049	30·7
Acetone	56·1	0·792	17·25
Benzene	80·5	0·879	25·7
Chloroform	61·2	1·483	38·8
Diethyl ether	34·6	0·714	21·6
Ethyl alcohol	78·3	0·789	12·0

B. CRYOSCOPIC METHOD

In this method the test sample is dissolved in a suitable solid organic solvent and the resulting depression of the melting-point of the solvent observed. The solvent should be easily crystallised and the solute should be easily soluble in the solvent. The solvent should be inert to the solute and the solute should not decompose at the melting-point of the solvent. The method becomes a simple one if solvents of high molecular melting-point depression constants, such as camphor and borneol, are used. In this case, the conventional melting-point method may be used, ensuring that superheating and changes in con-

centration of the mixture do not interfere, and a Beckmann thermometer is unnecessary.

APPARATUS

An ordinary melting-point apparatus is used (see *Determination of Melting-points*, p. 128). An Anschutz thermometer, with the proper temperature range (100° to 180° for camphor, 150° to 330° for borneol) and subdivided into 0·2°, is suitable for determining the temperature. For the bath, concentrated sulphuric acid or dibutylphthalate is used.

Solvents.—Camphor is the most popular solvent. It should be very pure and it is well to re-sublime about 10 gm. of it before use, keeping it in a well-stoppered wide-mouth bottle. Its melting-point, as well as its molecular melting-point depression constant, should be re-determined for every fresh sample of it, by using a known, pure solute, such as resorcinol. Wide variations in its constant, as well as in the constant of borneol, have been reported, presumably because of the different origins of the samples.

PREPARATION OF SAMPLE

Solids.—A thin-walled conical capillary (Fig. 29) is drawn from a piece of glass tubing of about 0·6 cm. internal diameter. In sealing its base a thick accumulation of glass should be avoided. This capillary (A) is wiped with a chamois and weighed after about 5 minutes. It should be handled with chamois-covered forceps or fingers during these operations. About 10 mg. of test sample are introduced into the capillary thus: The sample is placed on a small watch glass and taken up with another capillary (B) which fits into capillary A and has a fire-polished opening. The outside of B is wiped clean and then it is placed sufficiently down into A to effect a clean introduction, when the substance is pushed out of B with a thin glass rod. None of the material should remain on the side wall of capillary A. The capillary A is then re-weighed to obtain the amount of solute. About 100 to 200 mg. of solvent is introduced in the same manner with another capillary and capillary A re-weighed to obtain the weight of solvent.

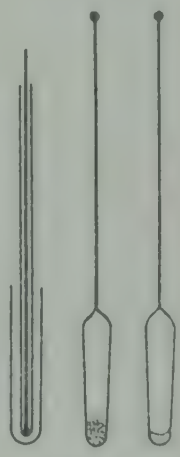

Fig. 29.

Liquids.—Liquids are introduced into the conical capillary by means of a suitable micro-pipette, taking care that no liquid solute is lost by evaporation or adhesion to the walls of the capillary. It may be advisable to introduce the solid solvent first and then the liquid solute.

METHOD

After the weight of the capillary, solute and solvent have been determined, the capillary is sealed thus: A glass rod of about 2 mm. diameter is placed in the capillary to within about 2 cm. from the bottom and the capillary heated in the non-luminous micro-bunsen flame, while being rotated, at the point where the glass rod touches the wall until the wall collapses. It is then withdrawn from the flame and drawn out to a thin glass rod about 5 cm. long. The capillary is then attached to the thermometer; the bulb of the thermometer is immersed completely in the liquid bath of the melting-point apparatus. The bath is heated with a micro-burner to a temperature sufficiently high to melt the contents of the capillary. After allowing the bath to cool to freeze the mixture of camphor and test material it is heated again to re-melt the mixture. The mixture should now be homogeneous. The mixture is again allowed to cool to the freezing-point and then it is heated slowly, at a rate no greater than 0·5° per minute, and the melting-point observed when the last crystal disappears, which is observed soon after the lattice of the crystals collapses and sinks to the bottom of the capillary. The cooling and melting are repeated until a check in melting-point to 0·3° is obtained. The melting-point of the solvent is taken under the same conditions to eliminate errors due to errors in the thermometer.

Calculation.—The molecular weight is given by:

$$M = 1000\,Kw/WD$$

where K is the molecular depression constant of the melting-point (see table below), w is the weight of sample taken, W is the weight of solvent taken, and D is the observed lowering of the melting-point.

Molecular Constants of Solvents

Substance.	*Melting-point.*	*Constant K.*
Camphor	176	40·0
Borneol	206	35·8
Camphene	49	31·1
Pinene dibromide	170	80·9

C. VAPORIMETRIC METHOD

The method to be described uses the Victor Meyer principle of determining the volume of vapour given by a known weight of the sample when it is vaporised. In order to overcome the difficulty of measuring the volume of vapour evolved by small weights of sample, the method to be described, due to Bratton and Lochte (16), uses the change in pressure of the system in which the material is vaporised, before and after the vaporisation, as an index of the molecular weight, the volume of the system being known.

APPARATUS

The apparatus (Fig. 30) consists essentially of a tube, A, in which the sample is vaporised by the heat from the outer jacket, B, in which the heating medium is boiled, and a mercury manometer, G, for measuring the increase in pressure within the vapour chamber, A, during the vaporisation. This chamber is constructed in Pyrex. Its wide central part is 20 mm. in diameter and 100 mm. long. To the bottom is fused a 40 mm. length of 4 mm. tubing and a 5-cm. length of 4 mm. tubing is fused to the upper end. Three short lengths of thin glass rod are sealed symmetrically round the circumference of the lower narrow part of the chamber, A, their lengths being such that the chamber is centred in the outer jacket.

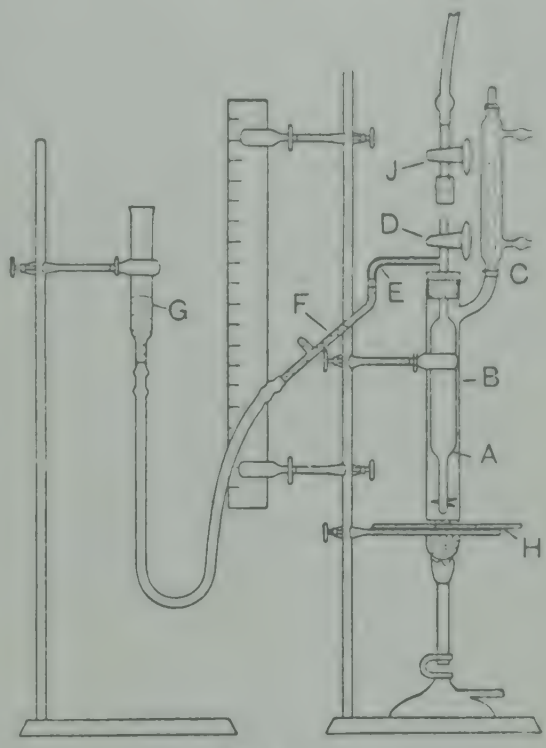

FIG. 30.

The outer jacket, B, consists of a Pyrex test tube, 20 cm. long and 3 cm. diameter. It has a side arm, C, sealed near its mouth; this side arm is bent as shown in order to serve as the inner tube of a condenser. This side arm is 20 cm. long and is constructed of 5 mm. Pyrex tubing.

A Pyrex tap, D, is sealed to the upper end of the vaporising chamber, B. This tap has a bore of 3 mm. and should be accurately constructed;. the bore of the key of the tap should be accurately aligned with the bore of the side arms when the tap is open so that nowhere along the length of the tap does the bore become narrower than 2 mm. A short distance below the seal of the tap to the vapour chamber is sealed a side arm, E. This is 8 cm. long and of capillary tubing of 0·5 mm. bore. The end is bent downwards as shown. To the end of the tube is sealed a piece of 5 mm. tubing, 10 cm. long, F. This tube is bent about 1 cm. below the point at which it is sealed to tube E. A mark is made on tube F about 0·5 cm. below this point of sealing to serve as a reference mark for the level of the mercury in the manometer. To the tube F is fused a short side arm, closed at its outer end; this is of 5 mm. tubing and is approximately 1·5 cm. long. This side arm serves to trap any air bubbles that may arise in the manometer tube.

Before the inner jacket is inserted into the apparatus, it is completely

filled with water to the reference mark and the water required to fill it weighed in order to ascertain its volume to this mark.

The end of the side arm F is connected by heavy rubber tubing to the levelling tube, G. This levelling tube contains a suitable amount of mercury in order that it may serve as a manometer.

The apparatus is assembled as shown. The outer jacket is supported in a hole in an asbestos board, H. The bottom of the outer jacket, B, projects to the extent of that part of it containing liquid ; the board prevents superheating of the vapour in the jacket. The vaporising chamber is supported in the outer jacket by means of a split cork stopper. A scale calibrated in mm. and 30 cm. long is supported vertically at a suitable position so that the position of the levelling bulb may be conveniently measured on it.

The diagram shows a tap, J, fitted with a short length of pressure tubing. This tap is used for experiments at reduced pressure.

METHOD

If the material whose molecular weight is to be determined does not decompose at atmospheric pressure (even at 20° to 30° C. above its boiling-point) the procedure is as follows : " Melting-point " capillary tubes are drawn out from soft glass tubing of about 1 cm. in diameter ; the tubing is drawn out to a diameter of slightly less than 2 mm. so that it will slip easily through the tap D. The capillary tubing is cut off into lengths of 5 cm. and the tube so obtained sealed at one end. The tube is dried and weighed on the balance to the usual accuracy. By means of a fine pipette a sample of 20 mg. is pipetted into the tube with a micro-pipette having a fine delivery tube. The tube is then heated gently 1 cm. from its mouth over a micro-flame to distil any liquid adhering to the tube at this point either into the lower part of the tube or into the open. The tube is now heated more strongly and is drawn out to a capillary. The upper end of the tube is heated with the pointed flame of a blowpipe until the tube closes and a bead of glass is formed of such a diameter that it will not pass through tap D. The upper end of the sample tube is now passed through the flame to remove any liquid that may still remain on it. The tube is cooled and re-weighed to obtain, by difference in weight, the weight of the sample.

For the heating medium, a liquid with a boiling-point about 20° above that of the sample is poured into the outer jacket of the apparatus to such a depth that it is at least 1 cm. below the bottom of the vaporising tube. The manometer is filled with mercury and the inner tube tilted to fill the trap on the side arm with the mercury. The inner tube is placed in position in the outer jacket, the tap closed and the burner under the jacket lighted. The liquid in the jacket is

boiled just vigorously enough to ensure that the jacket is always filled with vapour. To minimise condensation, the jacket may be wrapped with asbestos paper held in place with wire. With the liquid boiling at a steady rate, the mercury in the manometer is brought to the reference mark on the tube and tap D is closed. If the level drops, the steady state of boiling has not been reached; the tap is reopened until the vapour chamber has come to the temperature of the outer jacket. When no change in mercury level is observed on closing tap D, the determination may be started. The steady state is usually established within about 2 minutes from the heating liquid beginning to boil. Tap D is now opened and the sample tube inserted down it with the tube projecting into the vapour chamber and the bead resting on the upper end of the tap bore. The mercury level is brought to the reference mark and the level of the mercury in the levelling tube G is read on the scale to 0·2 mm. Tap D is closed to break the capillary of the sample tube; the tube drops to the bottom of the vapour chamber. As the sample vaporises, the levelling tube is raised to keep the mercury in the side arm approximately at the reference mark. When there is no further increase in the pressure in the vapour chamber, the mercury meniscus is adjusted to the reference mark and the level of the mercury in the levelling bulb again read on the scale. The difference in the first and the final levels of the mercury gives the change of pressure in the vapour chamber. The levelling-tube is lowered, the key of the tap D removed, a long capillary tube, connected to a suction pump, inserted into the vapour chamber, and the vapour in the chamber sucked off. The chamber is now removed from the outer jacket and the temperature of the vapour in the jacket is determined.

Determination at reduced pressure.—If the sample decomposes at its boiling-point, the initial pressure in the vapour chamber may be lowered to reduce the boiling-point to such a degree that decomposition no longer occurs. The pressure should be lowered sufficiently to ensure that the final pressure within the chamber is still low enough to prevent decomposition. Decomposition may be further hindered by filling the vapour chamber with inert gas. The auxiliary tap, J, is used in tests at reduced pressures. When the sample tube has been inserted in the tap D, the top of the tap, J, is lightly greased with vaseline and tap D connected to it by means of the pressure tubing. Tap J is closed and its pressure tubing connected to a vacuum pump. The levelling tube on the apparatus is sufficiently lowered to bring the mercury level in the side arm to a point just above the trap. The vacuum is applied and tap D is slowly opened; as the mercury rises in the side arm, the levelling tube is lowered until the mercury level is 10 to 20 cm. below the reference mark. Tap D is then closed and the mercury level brought to the reference mark. If the mercury level

does not remain constant the process is repeated. When it does remain constant, the level of the mercury in the levelling-tube is recorded on the scale. The sample tube is broken by turning tap D and the determination made as above. The calculations in this type of test are exactly the same as in the first.

Calculation.—If T is the absolute temperature of the vapour bath, m mg. the weight of sample taken, V ml. the volume of the inner jacket, as determined from the weight of water it holds when full to the reference mark, and p mm. the change of pressure within the vapour chamber, the difference in the first and final readings of the mercury level, then the molecular weight is given by:

$$\text{Molecular weight} = \frac{22410 \times 760 \times \text{T} \times m}{1000 \times 273 \times \text{V} \times p}$$

$$= \text{K}.m\text{T}/p$$

where $\text{K} = (62{\cdot}4\ \text{V})$ contains all the constants of the formula, including the volume of the inner chamber. This may be at once calculated when this volume is known.

The accuracy of the method is about $\pm$ 2 per cent. The determination requires about 20 minutes, the preparation and weighing of the sample requiring about 15 minutes and the vaporisation and measurement less than 5 minutes.

APPENDIX I

THE PURIFICATION OF SMALL AMOUNTS OF MATERIAL

The synthesis of organic compounds on a small scale—with the final product weighing about 100 mg.—is simpler and much more expeditious than their synthesis on the more usual laboratory scale, which yields a product weighing some 10 g. An advantage of micro-methods of analysis is that the products of small-scale syntheses may be submitted to most of the analytical procedures required to identify them. Moreover, micro-methods extend the usefulness of even large-scale syntheses for they enable small amounts of by-products, too small to be analysed by the normal methods, to be given a thorough analytical examination.

The purification of small amounts of a product before it is analysed is similar in principle to the purification of large amounts of material, but, in practice, the technique, like the technique of the synthesis, may be made simpler and naturally speedier. It may be worth while describing the techniques which have been suggested for purifying small samples of crude product. We have selected only a few of the suggested apparatus and those the simpler examples. It is doubtful whether, as a general rule, the more elaborate apparatus has any advantages over the simpler, though it may fill a need for special purposes.

In any method of purification, some losses of the material are bound to occur. Losses in solutions, which are discarded because recovery of the material in them would not repay the effort, are proportionately much the same whether 0·1 g. or 10 g. of material are purified, but mechanical losses—as occur, for example, in transferring material from one vessel to another—mount up on the smaller scale of working and may be serious enough to restrict the later investigation of the product. One of the chief aims, therefore, in treating small samples is to keep the mechanical losses as low as possible. In particular, there should be as few transferences as can be managed of the material from container to container. In fact, it is desirable to eliminate transference by submitting the material to all phases of purification in the one vessel, and, if possible, in the vessel in which the reaction leading to the product was conducted. For example, the reagents for the reaction may be mixed in a glass tube, the tube sealed and suitably heated to bring about the reaction, the tube opened when the reaction is complete and, after the material has been washed and digested with the appropriate liquid, the material may be crystallised in the tube after dissolving it in the appropriate solvent, or distilled into the cooled upper part of the tube. If the product is solid, the crystallisations

may be repeated to refine the product, the course of the purification being followed by melting-point determinations of a few crystals of the product. If the product is liquid, it may be distilled progressively in the tube, each droplet of distillate as it collects in the top part of the tube being submitted to a determination of its boiling-point in order to follow the gradual purification of the liquid. It may be impracticable to perform all operations in the one tube, but if transference of the material is unavoidable, simple and suitable forms of reactions vessels should be used so that the transference causes only the minimum loss of material.

GENERAL APPARATUS

For conducting reactions and some of the purifications, glass tubing, both of soft glass and of Pyrex, of 5- to 10-mm. internal diameter, should prove of service. Solutions are transferred from tube to tube by means of capillary pipettes. These pipettes should fit easily into the reactions tubes and should narrow down from about 3 to 4 mm. to about 2 mm. diameter. To make them, a length of 10 mm. glass tubing is drawn out in a batswing burner to the desired diameter and then cut off to a suitable length, say, 8 cm. for the wider part and 7 cm. for the capillary part. A rubber teat attached to the pipette enables liquid to be drawn into or expelled from the pipette by manipulating it appropriately. Narrow rods, fire-polished at both ends and about 3 mm. diameter, are required for the usual purposes.

A centrifuge, hand-operated or, preferably, electrically driven (of micro-size), is essential. One or two heating baths should be available. The heating baths are preferably small metal cylinders (copper or aluminium) heated by gas or an electrical winding and bored with narrow holes for the reception of reaction and other glass tubes. A convenient measurement of the blocks is 8 cm. high and 6 cm. diameter. If electrical heating is to be used, the electrical winding (about 1 metre of No. 28 nichrome wire) is wound over the lower 5 cm. of the cylinder in a spiral of 2·5 mm. pitch ; the wire is wound on a layer of asbestos paper or split mica wrapped round the cylinder. The last turns of the wire at the top and bottom should be twisted upon themselves to anchor the winding firmly to the cylinder and sufficient wire should be left over to allow connection to the source of current. The winding is additionally secured and thermally insulated to some extent by winding thick asbestos rope round the cylinder and over the winding. Morton (36) has a rim at the top of the block to allow the block to be suspended from a retort ring, the rim resting on the ring. For the electrically heated block, a rim of about 1·5 cm. width is suitable for this purpose. Otherwise, the block may be placed on the bench, the bench being protected by a sheet of asbestos composition. A rheostat

of a few ohms should be inserted in circuit with the winding to control the temperature of the block. Rather more elaborate heating blocks, which are also useful for melting-point determinations, have been described by Morton and Mahoney (37).

Other apparatus which is needed is described in the sections below and has been described in the body of the book.

METHODS OF PURIFICATION

The chief methods of purification are as follows:

1. Crystallisation of solids.
2. Extraction of solids and liquids by suitable solvents, either to dissolve the desired material from the impurities or the impurities from the desired material.
3. Distillation of solids and liquids and the sublimation of solids.
4. Drying, or in general, heating to drive off volatile impurities.
5. Purification by methods depending on adsorption phenomena.

The methods described below for making these types of purification apply to amounts of product to be purified of the order of 5 to 100 mg.

We have not listed purification by molecular distillation. This method has been chiefly used for the distillation of complex materials of high molecular weight; for example, such natural products as the vitamins. Though simple in principle, the method is rather elaborate in practice and for success the worker requires a fair experience with highly evacuated systems. It would serve little purpose to describe the method in any detail here and if the reader suspects that the method may be of some service in a problem of his own, he should refer to the publications on the subjects (for example, refs. 33, 34, 35).

In the methods depending on adsorption phenomena, we refer briefly to the decolorisation of solutions, contaminated, for example, by tarry material, and, more extensively, to chromatographic adsorption. We may say a few words here on chromatographic adsorption. Though it was first used some forty years ago, the method, like molecular distillation, has found fairly wide application only within the last decade or so. Again, like molecular distillation, it has been chiefly applied to complex, natural products. However, there is no reason why either should not find equally effective application to simple materials. Unlike molecular distillation, chromatographic adsorption requires only the simplest apparatus and no very advanced technique to succeed with it. A worker in the field finds few general principles, unfortunately, to guide him and much of his success will come from trial and error, helped by the work of others on materials similar to those which he proposes to separate. We do not propose

to write a description that will enable the unskilled to succeed with the method, but we have thought it of some value to give a summary of the method from which its principles and the simplicity of its operation may be judged.

1. CRYSTALLISATION

Crystallisation of a solid compound is best made by cooling a hot solution of it in a solvent in which its solubility in the cold is low. If a solvent cannot be found in which the material is very soluble when it is hot and hardly soluble when it is cold, the material has to be crystallised by allowing the solvent to evaporate from its solution. Alternatively, the material may be precipitated by adding to its solution a liquid in which it dissolves with difficulty.

Solutions often tend to become supersaturated with the material dissolved in them and the crystallisation is reluctant to start. The formation of crystal nuclei may be started from supersaturated solutions by such expedients as scratching the sides of the vessel beneath the solution or by seeding the solution, that is to say, adding a crystal of the material to be deposited or a crystal of a compound isomorphous with it. Freezing the solution is sometimes resorted to, but this is not always successful. The most favourable temperature for the start of the crystal formation may lie within a narrow range through which the cooling solution passes too rapidly to precipitate nuclei. Moreover, the most favourable temperature for the growth of the nuclei may be higher than that favouring crystal formation. Morton (36) suggests, therefore, that, if freezing is unsuccessful, the solution should be allowed to warm slowly and that, when once crystals begin to form, the temperature of the solution should be still further raised to encourage their growth.

Morton also points out that impurities present in the material to be crystallised tend to inhibit the crystallisation and, moreover, tend to lead to losses which could be avoided in their absence. It is desirable, therefore, to start crystallisation with relatively pure material and, in general, it will repay the effort to submit the product to a preliminary purification, as by ordinary or steam distillation, by extraction or by a preliminary drying.

APPARATUS

We have remarked that, if possible, the material should be purified in the tube in which the reaction leading to it has been conducted in order to eliminate losses caused by transferring the material. Glass tubes of, say, 0·6 to 1 cm. diameter area suitable for many reactions for any distillation or extraction to which the product may be first

subjected and also for its subsequent crystallisation. As a reaction and crystallisation tube, Wright (38) recommends the test tube with side arm shown in Fig. 31. The test tube (7·5 cm. long, 1 cm. diameter or 10 cm. long and 1·3 cm. diameter), of Pyrex glass, has a bulge blown upon its body 1 cm. below its flanged mouth and a side arm attached to one side of the bulge. Into the side arm is tamped a plug of long-fibred cotton wool and the mouth is closed by a cork (previously boiled), through which is inserted a short glass tube with its end (the end within the tube) pulled sharply to one side.

FIG. 31.

METHODS

The first step in the crystallisation is to examine the behaviour of the solid product in various solvents (if its behaviour in this respect is not known). When only small amounts of product are available, Wright suggests the following method, using a microscope slide for the tests. To a crystal of the product on the slide is added a drop of the solvent under test and, after observing its behaviour in the cold solvent, the crystal and solvent are heated by the simple method shown in Fig. 32. The slide is placed on the flat top of a large cork borer, which is mounted vertically; the stem of the borer is heated by a micro-flame and conducts the heat to the slide.

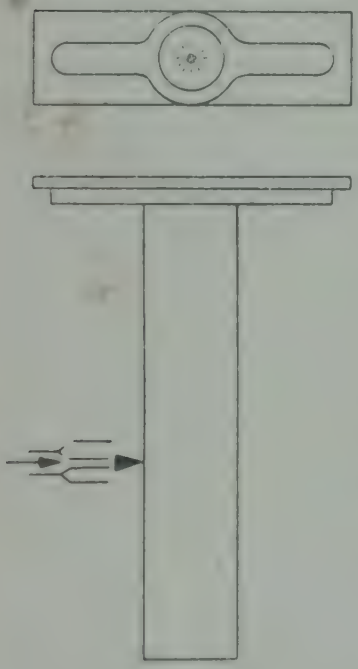

FIG. 32.

The drop of solvent may be applied to the crystal either from a micro-pipette or from the vessel illustrated in Fig. 33. One end of the glass tubing from which the vessel is made is drawn out to a thick capillary, the capillary bent to the shape shown and sealed off at its tip. The other end of the tube is drawn out roughly in the flame so that the constriction formed is about 0·5 cm. diameter and is at a point corresponding approximately to the final length of the vessel. The vessel is partially filled with the solvent and sealed off at the constriction. The capillary tip is then opened by filing off a fragment of the end. The vessel is manipulated by tipping it while holding it lightly in the hand and then, with the capillary tip just above the crystal on the slide,

FIG. 33.

a drop of the solvent is expelled by grasping it firmly to communicate the heat of the hand to the solvent.

The behaviour of each crystal in each solvent tested may be observed either with a hand-lens or on the stage of a low-power microscope; a magnification of some 15 to 20 is suitable. The behaviour of the crystal in the solvent both on the cold and on the warm slide should be noted, and the separation of the solid when it has dissolved in a solvent should be observed as the solvent evaporates; from a suitable solvent the material separates at the edge of the drop, leaving any impurity at the centre.

These preliminary tests may well include trials on mixtures of the common solvents, both uses to which they may be put being kept in mind, namely, (1) their use as a mixed solvent for the crystals to be refined and (2) the use of one liquid to dissolve the crystals and the use of the other to precipitate them from solution.

Before crystallising the bulk of the material from the reaction, any mother liquor from the reaction, or from any washing to which it has been subjected, is withdrawn from the crystals by the capillary pipette after centrifuging the mixture to pack the crystals at the bottom of the tube. A small amount of the chosen solvent is added and, if the material is to be crystallised by cooling its hot solution, the mixture is warmed in the heating block to somewhat below the temperature at which the solvent boils. The solution is then examined to see if all the solid has disappeared. If it has not, a further amount of the solvent is added to complete the solution. If an impurity resists the solvent, the solution must be filtered as follows: Somewhat above the level of the liquid (at a distance at which the liquid in the tube will not create difficulties in heating the tube in the flame) the tube is slightly constricted by rotating it round its own axis, with the part to be constricted heated in a small blowpipe flame, and allowing the walls to collapse a little. A small plug of purified asbestos is tamped into the tube to rest upon the constriction and is then held in place by making a second constriction just above it. The open top of the tube is sealed in the flame and the tube is centrifuged so as to force the solution through the plug, the solid residue remaining behind on the plug. That part of the tube containing the solution may be now cut from the other containing the filter plug and residue.

In order to crystallise the solution, it may be allowed to cool gradually; or if it is thought expedient to freeze it, it may be immersed in a suitable freezing mixture. If crystals do not readily form, one of the suggestions mentioned earlier—of scratching the sides of the tube, of seeding the solution with a crystal of the material laid aside for the purpose or, if the solution has been well cooled, of allowing it to warm—should lead to success.

In using the Wright side arm test tube, fitted as described above,

Wright proceeds as follows: A narrow-bore rubber tube, about 3 ft. long, is attached to the outlet tube in the mouth of the test-tube and a plug of cotton wool is tamped into the side arm. If the test tube has served as the reaction tube, the material may be given a prior digestion with a poor solvent and washed with a suitable solution. The solvent or solution is poured off through the side arm so that all the solid product is retained within the tube by the cotton-wool filter. For the crystallisation, a small amount of the chosen solvent is added, care being taken to wash any crystals on the cotton-wool plug into the tube: the cork with its glass tube is inserted into the mouth of the tube and the solvent refluxed gently by warming the tube in the heating block at a suitable temperature or over a hot plate or by holding it some 5 cm. above a micro-bunsen flame. Any solvent condensing in the tube in the mouth of the test tube should be blown gently out of it and back into the solution after wetting the plug in the side arm. It may be necessary to add more solvent to dissolve the solid completely. When dissolution is complete, the solution is poured off from any residue through the side arm into a second, warm test tube, the plug in the side arm filtering the solution. While pouring off the solution, sufficient pressure should be exerted on the mouth of the tube through the rubber tubing to keep it free from solution and to prevent the bulge on the test tube overfilling; at the same time, care should be taken to see that all the solution is forced out of the plug. The interior of the test tube is washed free from the solution by rinsing it with a few drops of solvent and pouring them off through the side arm. The material is then allowed to crystallise from the second test tube. Any residue from the product in the first test tube, and the crop of crystals in the second test tube, may be similarly treated to refine them.

Fig. 34.—Wright Condenser.

There is a certain loss of solvent when it is heated to dissolve the solid product and this loss has disadvantages when mixed solvents are used for the dissolution. It may be avoided by replacing the cork and glass tube in the mouth of the test tube by the small internal condenser shown in Fig. 34. The condenser is blown from tubing of 6 mm. internal diameter, the inner tube being of 2 to 3 mm. diameter.

For the final collection of the crystals, their suspension in the mother liquor is poured off through the side arm (the cotton-wool plug having been removed) upon a micro-Büchner funnel (of 1 to 1·5 cm. diameter) fitted with a filter paper. Alternatively, a sintered-glass filter funnel may be used for this final collection.

Blount (40) uses the apparatus of Fig. 35 in order to dissolve and crystallise solids products so that there is a minimum of transfer of solution and materials. The small condenser makes a ground-glass

joint with a small conical flask of suitable capacity, say 30, ml. A small sintered-glass funnel (porosity G2), without stem, is suspended from the condenser. The suspension consists of two platinum wires. One end of each wire is tied to one of the two glass loops fused to the upper rim of the funnel and the other end is hooked into one of the two holes near the bottom of the condenser stem. The crystals from the reaction are first filtered through the funnel, which, for this operation, is supported in a glass adapter attached to a suction flask. The filtration may be expedited by applying suction. After washing the product, the funnel is wiped clean and then hung from the condenser, the solvent from which the material is to be crystallised placed in the conical flask, the apparatus assembled and the solvent gently refluxed to dissolve the crystals upon the funnel as it drips from the condenser. The solution in the flask is allowed to crystallise and the crystals are again filtered through the funnel from which they may, if desired, be re-dissolved and re-crystallised.

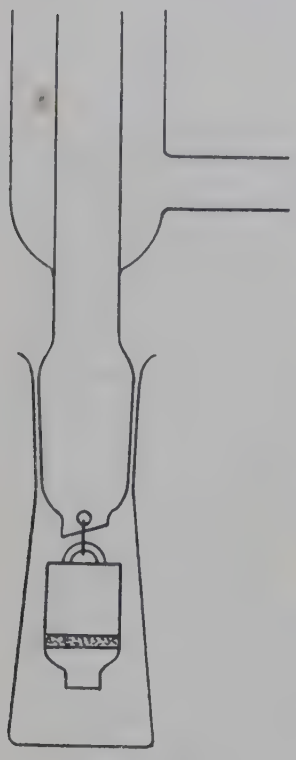

FIG. 35.

The melting-point of the product should be followed throughout the repeated re-crystallisation by the usual melting-point determination on a few crystals of the dried product.

Of the above techniques, the crystallisation in the tube and in Wright's side arm test tube appear to be the best because of their simplicity and the restriction of the operations—the reaction * (as a rule), the washing, any digestion that may be made to effect a preliminary purification and the ultimate crystallisation—to one vessel.

2. EXTRACTION AND DIGESTION

Solid material may be extracted or digested in a reaction tube to purify it of at least some of its impurities by adding the chosen solvent for the impurities (a poor solvent, of course, for the product to be purified) to the product in the tube (after centrifuging and withdrawing any liquid or solution from the tube), warming it in the heating block and, after digestion, withdrawing the solvent from the tube by means of a capillary pipette. If Wright's side arm test tube is used, the digestion may be made with the tube closed by the micro-condenser. The extracting solvent is poured off through the side arm which is

* Wright's paper should be consulted for a typical use of his side arm test tube as a reaction tube.

plugged with cotton wool to act as filter. After washing and drying, the product may be submitted to crystallisation. The use of Blount's apparatus for extraction is obvious.

Among other extraction apparatus which have been devised may be mentioned the following: The Wasitzky apparatus is shown in Fig. 36. It is essentially a Soxhlet apparatus on a small scale. The material, in a filter-paper thimble, is extracted by the intermittent flow of condensed liquid through it; when the thimble fills with condensate, the siphon attached to the tube supporting it drags the condensate through the thimble and ejects it into the solvent boiling in the flask. Browning (39) and Titus and Meloche (41) have devised similar extractors. That of Titus and Meloche is shown in Fig. 37. The apparatus was designed

FIG. 36.

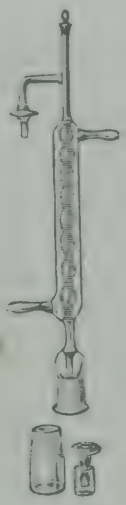

FIG. 37.

for the quantitative determination of extractable material in a micro-sample. The apparatus consists essentially of a cup from which the solvent is refluxed, a condenser making a ground-glass joint with it, and a glass extractor thimble which has hooks sealed upon it by which it is supported from an aluminium ring resting on the rim of the cup. The filter paper, supporting the material to be extracted, is clamped into position between the extractor thimble and a lower glass tube which fits into the thimble by an internal ground joint. The solvent for the extraction is placed in a weighed dish which is placed within the cup. If desired, the apparatus may be partially evacuated for the extraction through the side tube at the top of the condenser. After evacuation, the tap on the side arm is closed and heating begun. For low-boiling solvents, an electric light bulb is a convenient source of heat. After extraction, the solvent is evaporated from the solution in the weighing dish by restoring the vacuum within the apparatus. When the solvent has disappeared, the apparatus is carefully filled with air, dismembered and the dish again weighed to

determine the amount of extract. For fuller details of the method of using the original papers should be consulted.

Liquids (liquid products or the solutions of a liquid or solid product) are normally extracted by means of a liquid immiscible with them in a separating funnel. (More elaborate methods for the automatic and continuous extraction of liquids have been devised, but it is doubtful whether they would repay adaptation to small-scale work.) The ordinary separatory funnel is a crude instrument for micro-scale work ; the tap on the funnel leads to losses of the liquid. Browning (39) illustrates a tapless separatory funnel (Fig. 38). All the liquids dealt with are sucked into the separation chamber through the capillary. For example, in extracting an aqueous solution by means of ether, the solution is drawn into the extracting chamber by applying suction with the mouth to rubber tubing attached to the top of the chamber. The ether, say, about 2 to 3 ml., is then drawn into the capillary, the two layers shaken together and then allowed to separate by standing. The lower layer is removed by a gentle blow, this layer being ejected until the meniscus reaches the capillary tip. On releasing the pressure, the upper layer of ether solution retreats into the bulb. It may be washed by drawing into the apparatus the appropriate solvent, shaking and ejecting the solvent as above. Further aqueous solution may be then added to be extracted.

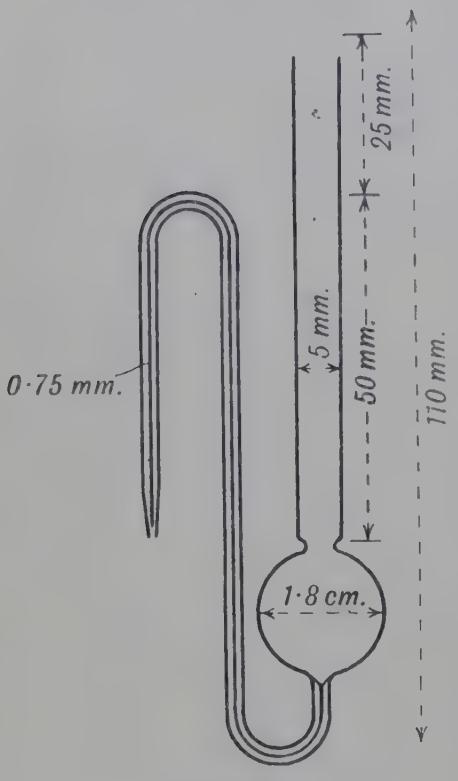

FIG. 38.

3. SUBLIMATION AND DISTILLATION

Sublimation of solids and the distillation of liquids are so akin that the same simple apparatus may be used for each.

If the sublimation of a solid product is contemplated in order to purify it, the possibility that it can be sublimed must be verified, of course, by a preliminary test on a few grains of the product. This small sample of the product, centrifuged to the bottom of a small tube, is gently heated over a micro-flame so that it may sublime upon the upper, cool surface of the tube. If this test proves to be satsifactory, the bulk of the material in the reaction tube is centrifuged to the bottom of the tube, any tarry material on the sides is worked into a capillary

or on to a thin glass rod which is dropped into the tube, and the tube is placed in the cold heating block. A piece of wet filter paper is wrapped round the upper part of the tube to act as condenser for the sublimed vapours. If desired, the tube may be connected to a vacuum pump, for example, a rotary oil pump, and kept evacuated during the sublimation. The tube is gradually heated by closing the electric circuit to the heating block, and when the material begins to sublime the block is kept fairly well to the temperature it has attained. When the sublimation is complete, the tube is withdrawn from the block, any vacuum that has been applied is broken, that part of the tube containing the sublimate is cut off somewhat below the point where the sublimate rests, and its end sealed in the flame with the tube inclined downwards so that the heat does nor appreciably affect the sublimate. The melting-point of the sublimate may be taken on a few crystals extracted from the tube and the sublimate further purified by crystallisation in the tube.

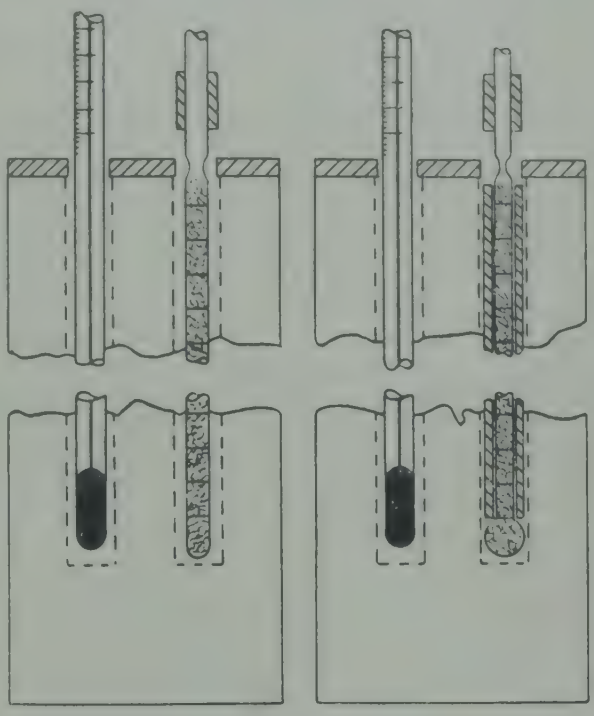

Fig. 39.

The distillation of a liquid product in the tube is very similar to this sublimation. The gradual purification of the liquid during the distillation may be followed, however, by distilling it only gradually, a droplet at a time, and by determining the boiling-points of the successive droplets until the boiling-point becomes stable. The tube should be slightly constricted at a point on its cooler length, the filter-paper condenser being placed just above the constriction so that the distillate is caught in the constriction. It is best to fill that part of the tube to be heated with glass wool or purified asbestos wool, and to make sure, before the distillation, that the liquid to be distilled is at the bottom of the tube, by centrifuging it.

Morton and Mahoney's description of their rather more refined procedure will make the method clear (37). They use the two types of tube shown placed in a heating block in Fig. 39, preferring the second type with the small bulb on its base ; it is more capacious and for the same amount of liquid distilled there is a longer fractionating column above the surface of the liquid. The tubes for the fractionation

are about 4 mm. diameter and 14 cm. long; they are conveniently drawn from glass tubing of 15 mm. diameter. The tubes are constricted near the top in a blowpipe flame after packing them with glass wool or purified asbestos wool. The glass wool should be ground in a mortar before inserting it into the tube. The constriction in the tube should be as short as possible so that a minimum of condensate is collected. A condenser, consisting of a piece of wet filter paper, is wrapped round the tube just above the constriction. The heating block (copper or aluminium) is 4 cm. square and 15 cm. high. Two holes, 8 mm. diameter, are bored in it to a depth of 9·5 cm. The thermometer in the one hole facilitates control of the distillation. The fractioning tube in the second hole is surrounded by a glass tube which partially insulates it from the heating block. A sheet of asbestos, 1 mm. thick, covers the upper surface of the block and prevents the " condenser " part of the fractionating tube becoming too hot. The block may be heated either by a small glass flame or by an electrically heated nichrome winding (see p. 144).

A drop of the liquid to be examined is pipetted into the tube, which is then centrifuged to force the drop through the constriction to the bottom of the capillary. The wet paper condenser is attached, the glass insulating jacket is put in place on the tube and the tube is inserted into the heating block. Heat is applied gradually. The filter paper may be further cooled by directing a fine stream of air against it. When the ring of distillate reaches the constriction and the first tiny droplet appears above it, the heating of the block is interrupted, the asbestos cover is pulled aside and the fractionating tube removed and centrifuged for several minutes. The insulating jacket is also removed and cooled. After centrifuging for a few minutes, during which time the block will have cooled by about 4° C., the fractionating tube is replaced with its jacket in the heating block and the liquid in the tube again distilled as above. This procedure of distilling a droplet of the liquid is repeated a few times; the lowest temperature at which sufficient liquid for a determination of its boiling-point will condense in the constriction in about a minute is noted. After this repetition, the next droplet which is distilled into the constriction is sampled for a determination of its boiling-point. For this purpose a number of Emich boiling-point tubes are prepared (p. 130) by drawing out 1 cm. glass tubing to a diameter of about 1 mm. and further drawing out this capillary at a convenient point to a fine tip, about 1 cm. long and 0·2 to 0·5 mm. diameter. The 1-mm. capillary is then cut off to a length of about 10 cm. to complete the tube. To sample the distillate, the fine tip of the boiling-point capillary is touched to the droplet until a small amount is drawn up by the capillary attraction into the tip. The fine tip is then sealed in a micro-flame so that a small bubble of air is trapped in the tip below the droplet in it. The capillary is trans-

ferred to a heating bath or a heating block provided with a thermometer and, in the usual way of determining the boiling-point, gradually heated: the ascending droplet in the tube is observed until it reaches the surface of the liquid in the heating bath or the top of the heating block, when the temperature of the bath is noted. This is the boiling-point of the droplet.

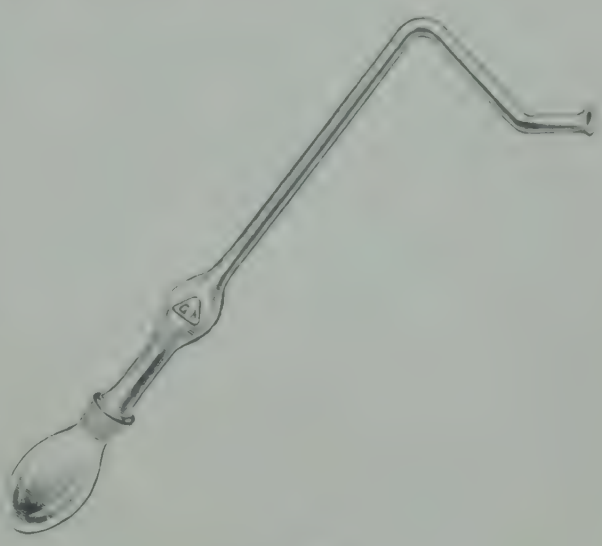

FIG. 40.

After the droplet has been sampled and the boiling-point capillary has been inserted in the boiling-point apparatus, the fractionating tube is withdrawn from its heating block (the heat to which has been interrupted) and centrifuged. The insulating jacket is also withdrawn so that it may cool. When the boiling-point has been determined, the centrifuged tube is again placed in its jacket and reinserted into the heating block, which will have cooled somewhat (by not more than 2° C. for rapid work) and the fractionation is continued. With care, all operations can be so timed that the boiling-point of one droplet can be determined before collecting the next. When once the boiling-point has become stable, the distillation of the main product can proceed and the total distillate withdrawn by, for example, a capillary pipette.

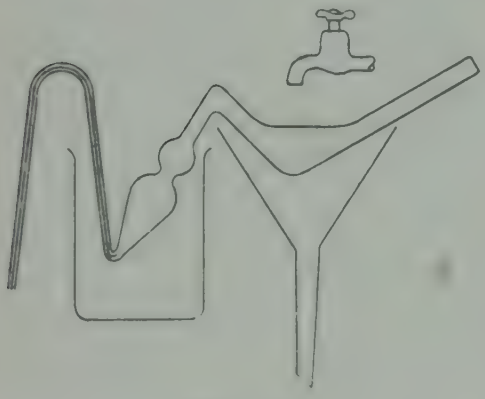

FIG. 41.

Benedetti-Pichler uses the apparatus shown in Fig. 40. It was designed for the distillation of a few ml. of liquid, especially of an aqueous solution. The bulb has a capacity of about 10 ml. The long condensing tube gives a fair degree of fractionation. Bumping during the heating is prevented by the addition of some zinc dust. Distillate is collected in the crook of the condensing tube which is encircled with wet filter paper. The course of the distillation can be followed, of course, by determining the boiling-points of successive fractions.

Wright uses the distillation apparatus shown in Fig. 41, which is designed for amounts up to 100 mg. of liquid. It is made from

tubing of about 5 mm. diameter. The liquid is introduced into the chamber by dipping the capillary into the liquid and applying suction at the other end through rubber tubing. If the liquid is in solution in a volatile solvent, the solvent may be driven off by heating the chamber in a beaker of hot water and carefully evacuating the system. When the liquid has been introduced and any solvent has been evaporated, the capillary is sealed while applying a moderate vacuum. Full vacuum (of a rotary oil pump, for example) is then applied and released so that most of the capillary becomes filled with liquid. If the liquid is to be distilled under a partial vacuum, the necessary vacuum is arranged by means of a manometer and an adjustable leak (for example, a needle valve) in the vacuum line leading to the still. A plug of cotton wool is tamped into the tube and prevented from being drawn into the vacuum line by trapping a few strands of it between the rubber connection to the vacuum chamber and the outside of the tube. The receiver may be cooled by a stream of water, which is carried away by a filter funnel, or by a dish containing ice or mixture of solid carbon dioxide and ether. After adjusting the vacuum, the chamber is gradually heated in an oil bath until the capillary empties itself; this represents the initial boiling-point of the liquid under the applied vacuum. If the liquid is to be fractionated, the vacuum is slowly broken, the cotton-wool plug is withdrawn and the fraction collected is removed in a capillary pipette. Its boiling-point is determined under atmospheric pressure if desired. The capillary is then broken, re-sealed under a moderate vacuum and the distillation continued as before.

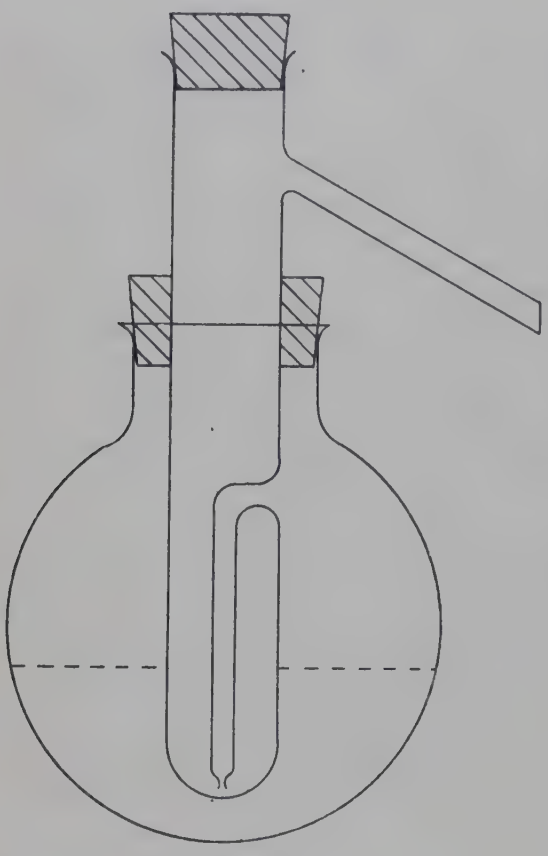

FIG. 42.

Steam distillation.—If it is desired to distil small amounts of a product in steam, Escot's apparatus (Fig. 42) is useful. The steam is generated from the water in the flask. If the product is difficult to distil and, in any event, in order to expedite the distillation, it is of

advantage to generate the steam from a saturated solution of common salt. Bumping may be prevented by any of the well-known methods, for example, by adding pieces of porcelain tile or by packing the flask with glass wool to a level slightly above that of the water. The product to be distilled is contained in the inner tube and the vapours of the product and steam are led by way of the side arm to a condenser and receiver.

4. DRYING

Material may be dried in a tube or in Wright's side arm test tube by inserting it, with the material centrifuged to the bottom, in a heating block, maintained at the proper temperature (somewhat below the melting-point of the material) and blowing air over the surface of the solid, the air being supplied through a capillary held in the tube so that its lower end is just above the material. For drying solids caught on such containers as Büchner and sintered-glass funnels, a small oven is suitable. Placing the tube or oven under vacuum during the heating expedites the drying. If it is undesirable to heat the product, it may be dried in an evacuated desiccator loaded with a desiccant which will absorb the vapours of the contaminating liquids, for example, calcium chloride for water and alcohols, concentrated sulphuric acids for water and bases, solid caustic soda for water and acids, paraffin wax for such organic solvents as ethers and benzene.

5. PURIFICATION BY ADSORPTION PROCESSES

A. Decolorisation of Solutions

A preliminary purification of a solution adulterated and coloured by tarry products, as many solutions of synthetic products are, may be made by allowing active carbon to adsorb the contaminants. This common practice for the partial purification of large amounts of product can be equally applied to micro-scale syntheses. The active carbon should be added to the solution only a little at a time, the mixture boiled or refluxed, filtered and the decolorisation of the filtrate continued in the same way if this is still contaminated. The increasing purification of the solution should be followed by filtration until a colourless or clear filtrate shows the purification is complete.

B. Chromatographic Adsorption

Chromatographic adsorption is still largely an art, but may offer a means of separating mixtures of materials which the commoner methods find intractable. The following remarks on the method are intended merely as an introduction to it. If the reader, unfamiliar with the subject, suspects that the technique might solve a difficulty

for him, he should refer to the books by Zechmeister and Cholnoky (43) and Strain (44).

The separation of a mixture of materials in solution by this method depends on differences in their adsorption on a suitable adsorbent. The adsorbent is used in the form of a column down which the solution to be resolved—*chromatographed*—is poured. The solutes are adsorbed near the top of the column, forming a coloured band there. As the more strongly adsorbed solutes are the first to be adsorbed, they are retained nearer the top of the column. In order that they can be easily isolated from one another, the bands are now separated widely by pouring a solvent down the column ; this solvent may be the same as the solvent in which the adsorbed materials were originally dissolved, or another. The effect of this washing, this *development* of the *chromatogram*, is to carry the coloured bands gradually down the tube, and, on its course, increasingly separate the components of the band. The more strongly adsorbed bands are carried down the column more slowly than the more weakly adsorbed, since they dissolve only reluctantly in the solvent " developer " and are rapidly readsorbed as their solution falls down the column. In time, the fully developed chromatogram will appear in the column of the adsorbent as a series of relatively narrow coloured bands, distributed along the column and separated by uncontaminated adsorbent. The bands are then each isolated from the column, either by cutting the glass tube at the bands or by forcing the column from the tube and dissecting it outside the tube. Finally, the material adsorbed in each band so separated is extracted from the adsorbent by means of a strong solvent.

This simple method is only successful when the adsorbed materials are coloured or otherwise readily seen. When they are colourless, the separation of the bands creates some difficulties which may perhaps be overcome by one or other of several methods. The clumsiest expedient is to cut the column into many sections, examine the composition of the material (if any) adsorbed on each section, repeat the chromatography on the solution under the same conditions as to volume of solution and developer used, and to cut the column in a way suggested by the results of the first trial. If the compounds fluoresce in the ultra-violet, the column may be examined and dissected in the light of a mercury-vapour lamp. If coloured derivatives of the solutes can be prepared, their solution may be chromatographed. Other expedients are (a) to develop colours on the colourless bands on the column after extruding it from the tube by brushing a reagent solution along the column ; (b) to develop colours on the colourless bands by pouring down the column the solution of a suitable reagent ; (c) to use Trappe's method (45) of adsorbing the solution on silica gel and darkening the bands by means of a suitable solvent.

As well as resolving a mixture into its components, chromatography

may be used to purify a crude material and to test the homogeneity of a product. In purifying a material, the technique is simplified in that the subsidiary bands—those of the impurities—may be rejected or washed out of the tube and the main band repeatedly worked up. As regards the testing of the homogeneity of a product, homogeneous material deposited on the adsorbent will pass down the column, as a rule, as one band when the column is developed; if a solution gives one band only, it is fairly safe to conclude that only one compound is present. There are rare exceptions to this rule. On the one hand, the components of a mixture may pass down the column together. If there is no segregation in a certain chromatogram, some confirmation that only one material is present may be obtained by trying other adsorbents and other solvents. If no separation is then obtained, it becomes difficult to resist the conclusion that only one compound is present. On the other hand—an even rarer occurrence—one component may separate into two or more zones, owing, for example, to decomposition in the column.

APPARATUS

The simplest apparatus consists of a tube of suitable dimensions, for example, 40 cm. long and 2 cm. wide for separations on the macroscale, or 20 cm. long and 0·5 cm. wide for separations on the microscale, is secured to a suction flask by a rubber stopper. The lower end may be drawn out to offer a shoulder on which rests a plug of cotton wool to support the column of adsorbent in the tube. It is more convenient to have the glass tube containing the column of adsorbent make a ground-glass joint with an adapter which is inserted into the rubber stopper of the suction flask. In this tube, the column may be supported on cotton wool which itself is supported on a perforated porcelain plate resting in the tube at the ground joint.

METHOD

It is possible to use a variety of adsorbents and of solvents, both for the solution from which the materials are to be adsorbed and for the development of the chromatogram, though the choice of solvent is also governed by the solubility of the materials. There are no general rules for choosing the most advantageous adsorbent and solvents, though some guide may be obtained from the literature on the successful chromatography of similar materials. A small-scale preliminary test may be suggestive. Crowe (46) has described such a test. A number of adsorbents to be tested are placed in the cups of a spot plate (about 1 to 2 g. of each suffice) and are moistened with various solvents; or 2 to 3 drops of a creamy mixture of each of the adsorbents in the

solvents may be used. One or two drops of the solution to be tested are then placed in the rim of each cup and allowed to flow into the adsorbent. From these trials, the most suitable combination of adsorbent and solvent is determined for the solution to be chromatographed.*

An adsorbent commonly used is activated alumina, which, before use, should be closely sized by sieving, for example, between the 40- and the 60-mesh (B.S.I.) sieves. Other adsorbents that have found use are calcium carbonate, calcium hydroxide, gypsum, magnesium oxide, fuller's earth and silica gel.

Most of the common organic solvents, such as ether, petroleum ether, the lower alcohols, benzene, have been used for one material or another, both for the solution of the material and the development of the chromatogram. The concentration of the solution should be of the order of 0·01 per cent. and sufficient of the developing solvent should be used to give a wide separation of the bands so that they can be recovered uncontaminated by other bands.

The first step in the process, the preparation of the column, may be done in two ways. The glass tube may be packed either with dry adsorbent or with a suspension of the adsorbent in the solvent (in which, of course, it should be insoluble) used to dissolve the materials to be separated. The column should be uniformly packed ; no cracks or channels should be left in it through which the solution can run more or less freely. If the dry material is packed, it should be added a little at a time, each addition being tamped down with a glass rod before adding further amounts. If the adsorbent is added as a suspension, a little of the suspension is added at a time, slight suction being applied after each addition to pack the adsorbent down ; but in doing so, the adsorbent should be kept submerged in the solvent. In either case, the tube is filled about three-quarters full, the upper quarter being left empty for later reception of the solution undergoing treatment.

Before treating the solution in a column prepared dry, the column is moistened with the solvent introduced from a dropping funnel at the top of the column. The solution to be treated is then poured through the adsorbent from the dropping funnel at such a rate that the whole of the column is kept immersed in the solution.

After the solution has passed, the chromatogram is developed by allowing copious amounts of a suitable solvent to descend the column

* Crowe also describes a neat micro-method of chromatography. A glass Petri dish, about a quarter-full of the chosen adsorbent, is gently shaken into an inclined position so that the adsorbent in it settles as a wedge, very thin at the upper edge and a few millimetres thick at the lower. The solution to be analysed is dropped from a 1-ml. pipette into the centre of the dish, which is held in a tilted position so that the solution may flow slowly downwards through the adsorbent from the thin edge of the wedge. The solvent is added slowly drop by drop to form broad zones of separated material.

from the dropping funnel. If the zones descend only slowly with the solvent, it may be advisable to try another solvent to accelerate their fall. The developing solvent, like the solution, should be supplied at such a rate that the adsorbent is kept submerged. The development should be continued until the zones are well marked and well separated.

After development, suction is applied to the column through the suction flask to denude the column of liquid and the adsorbent is then extruded from the glass tube. This is the part of the process requiring most skill and experience. The adsorbent should not be too dry when extrusion is attempted. The column is first loosened from the tube by letting it fall upon the bench from a height of a few centimetres. (Its fall should be broken by placing a cloth on the bench.) When the column has moved a short distance in the tube, it may be pushed out of the tube by means of a wooden or glass rod.

The column of adsorbent is then cut with a spatula, working from each uncontaminated part towards each band, and scraping off this part until the surface of each band within the bulk of the adsorbent is laid bare.

As soon as a band is separated, it is at once dropped into a beaker of the solvent for extracting the adsorbed material, dissolved by stirring or heating, the solution filtered from the adsorbent and the solute recovered in any suitable way.

To separate colourless bands, the devices mentioned earlier (p. 158) may be tried. For details of the procedure the reader may be referred to the books available on the subject and already mentioned.

APPENDIX II

PREPARATION AND STANDARDISATION OF VOLUMETRIC SOLUTIONS

0·025 N HYDROCHLORIC ACID SOLUTION

An accurate standard acid of the necessary strength may be obtained as follows: Concentrated hydrochloric acid is diluted with distilled water to a density of 1·1 (determined with a hydrometer). This diluted acid is then distilled at a speed of about 3 to 4 ml. per minute. The first three-quarters of the distillate is rejected and most of the last quarter of constant-boiling mixture is collected in a dry flask. About a litre of the diluted acid should be taken for the distillation. The distillation is discontinued when about 50 ml. of acid remain in the distillation flask. The barometric pressure should be read at the beginning and end of the collection of the constant-boiling distillate, and the average taken of these two readings. The following weights of the acid appropriate to the atmospheric pressure prevailing during the distillation are taken and diluted to 1 litre to furnish exactly 0·025 N acid.

Atmospheric pressure during distillation, mm.	730	740	750	760	770	780
Weight of distillate, gm., to give 1 litre of 0·025 N acid	4·4888	4·4942	4·4995	4·5048	4·5102	4·5155

The weight appropriate to intermediate pressures is easily obtained by interpolation since the relation between the weight of distillate required and the atmospheric pressure may be regarded as linear over the restricted range of pressure given above.

The acid is weighed in a dry, stoppered conical flask to the nearest 0·5 mg. weight. The weight may be adjusted without much inconvenience by removing acid from or introducing it into the flask by means of a capillary pipette so that a solution exactly 0·025 N is obtained after dilution.

The constant-boiling acid may be kept unchanged for long periods in a well-stoppered bottle.

If no constant-boiling acid is available, an approximately 0·025 N acid may be obtained by diluting 3 ml. of concentrated acid to 1 litre. This standard acid, of course, requires calibration.

Standardisation of hydrochloric acid.—Titrant acids are commonly standardised by means of sodium carbonate, but a more convenient standard is borax, $Na_2B_4O_7$. 10 H_2O. Hydrated salts are difficult

to dry without affecting their water of hydration, but the following method of preparing pure borax (Hurley (33)) obviates any difficulties in this respect. Borax of analytical purity is dissolved in hot distilled water in the proportion of 30 gm. per 100 ml. water. At this concentration, no crystallisation occurs above 55°, thus avoiding the crystallisation of the pentahydrate; the transition between the two modifications of the hydrated salt is 61° C. The solution is cooled. The crystals are filtered with suction in a large sintered-glass funnel, freed from the mother liquor by suction, washed with two small portions of water, then two portions of absolute alcohol and finally two portions of ethyl ether. These organic liquids are applied per washing at the rate of 5 ml. per 10 gm. of crystals. The washed borax is then spread out in a thin layer on a large watch glass and allowed to stand at room temperature to allow evaporation of the ether. The borax may be kept for a long time in a *tightly closed* bottle without appreciable change in its composition.

For standardising the hydrochloric acid the required amount of borax (equivalent weight, 190·71) is weighed to 0·1 mg. to give a litre of solution of 0·025 N strength, and 25 ml. of this solution titrated in triplicate with the acid to be standardised, using the mixed indicator (p. 89) for detecting the end point.

0·025 N SODIUM HYDROXIDE SOLUTION

A concentrated solution of the pure caustic soda is first made by dissolving 50 gm. of pure sodium hydroxide in 50 ml. of distilled water in a Pyrex flask. Any sodium carbonate in the hydroxide remains in suspension and is filtered off through a sintered-glass filter funnel; during the filtration the mouth of the funnel is closed by a rubber stopper through which is inserted a tube of soda-lime to keep carbon dioxide away from the solution. 1 N solution is made by weighing out approximately 10 gm. of the concentrated solution in a 100 ml. conical flask and diluting to 500 ml. in a volumetric flask. For the purpose of diluting the concentrated solution, distilled water, recently boiled for a few minutes, should be used. Of this solution, 25 ml. are in turn diluted to 1 litre with freshly boiled distilled water. The solution is stored in a bottle with a rubber stopper and should not be unnecessarily exposed to air.

Standardisation.—The solution may be standardised against the 0·025 N hydrochloric acid prepared from constant-boiling acid, which may be regarded, therefore, as a standard, or, if this acid is not available, against potassium bi-iodate. The potassium bi-iodate is purified by two recrystallisations from water and dried by heating to constant weight at 110° C. For the standardisation, approximately 0·4 g. of

the potassium bi-iodate, accurately weighed to 0·1 mg. into a small conical flask, is dissolved in about 20 ml. of water and titrated from a 50 ml. burette with the sodium hydroxide solution, using the mixed indicator (p. 89) to detect the end point. The equivalent weight of potassium bi-iodate is 389·9.

0·025 N BARIUM CHLORIDE SOLUTION

3·054 g. of barium chloride dihydrate (A.R. quality) are dissolved in freshly boiled, distilled water and the solution brought to a total volume of 1 litre in a volumetric flask. The solution may be regarded as a primary standard. It may be standardised, if thought desirable, by precipitating the barium from a measured volume of the solution by adding a solution of sodium sulphate in excess, and weighing the precipitated barium sulphate. The authoritative text-books, for example, Kolthoff and Sandel's *Text-book of Quantitative Inorganic Analysis* (New York, 1937) should be consulted for the details of this determination.

0·05 N AND 0·02 N SILVER NITRATE SOLUTIONS

0·05 N and 0·02 N silver nitrate solutions are prepared by dissolving 8·4944 g. and 3·3978 g. respectively of the pure salt to 1 litre of solutiom in water. The freshly prepared solution may be regarded as a primary standard. The solutions may be standardised from time to time by titrating them against an accurately weighed amount of about 50 mg. of purified potassium chloride which has been dried at 140° C. The titration should be done using dichlorofluorescein as indicator (p. 104). When the weight burette is used the silver nitrate should always be standardised against potassium chloride.

0·025 N POTASSIUM DICHROMATE SOLUTION

1·2258 g. of potassium dichromate (A.R. quality), previously dried at 150° C., is dissolved in distilled water and the solution made up to 1 litre in a volumetric flask. The solution may be regarded as a primary standard.

0·025 N FERROUS AMMONIUM SULPHATE

9·8 g. of the salt are dissolved in about 200 ml. of distilled water, 25 ml. of concentrated sulphuric acid added and the solution finally brought to a volume of 1 litre in a volumetric flask. The solution must be standardised before use by means of the potassium dichromate solution. To 25 ml. of the ferrous solution in a conical flask, diluted to about 100 ml. with water, 1 ml. of concentrated sulphuric acid and

3 ml. of 85 per cent. phosphoric acid are added and about 5 drops of indicator, a 0·2 per cent. solution of barium diphenylamine sulphonate in water. The solution is titrated slowly with the dichromate solution, especially near the end point, when the colour change from green to purple appears.

0·025 N SODIUM THIOSULPHATE SOLUTION

6·2 g. of sodium thiosulphate are dissolved in boiled distilled water, the solution cooled, 0·1 g. of sodium carbonate or 0·5 ml. of chloroform added as preservative, and the solution finally brought to a volume of 1 litre. After allowing the solution to stand 24 hours, it is standardised by means of the standard dichromate solution as follows: To 25 ml. of the potassium dichromate in a conical flask, 1 g. of potassium iodide and 4 ml. of concentrated hydrochloric acid are added, the solution mixed by shaking and the liberated iodine titrated with the sodium thiosulphate solution, this iodine being equivalent to the potassium dichromate used. The titration is continued until the solution becomes a yellow-green, starch solution indicator (p. 110) is added and the titration is continued to the end point, a change from the blue of the starch-iodine complex to the light green of the chromium salt solution.

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